Advanced Processing Considerations for Lithium-Ion and Polymer Electrolyte Fuel Cell Electrode Coatings

• Presented by: Marissa Wood
  Oak Ridge National Laboratory

October 29th, 2018
• Overview of R2R Collaboration Between National Labs and Industry

• R2R Coating of Thick Structured Electrodes for High-Energy-Density Li-Ion Batteries
  • Conclusions/Future Work

• Single-Process R2R Coating of Gas Diffusion Electrodes for Polymer Electrolyte Fuel Cells
  • Conclusions/Future Work
Overview of Advanced Manufacturing Technology Areas

Advanced Manufacturing for Energy Systems

- Electric Power Delivery
- Electric Power Generation
- Fuels Production
- Buildings
- Transportation

Advanced Manufacturing Technology Areas

- Sustainable Manufacturing - Flow of Materials through Industry
- Combined Heat and Power Systems
- Waste Heat Recovery Systems
- Advanced Sensors, Controls, Platforms and Modeling for Manufacturing
- Process Heating
- Process Intensification
- Roll-to-Roll Processing
- Critical Materials
- Direct Thermal Energy Conversion Materials, Devices and Systems
- Wide Bandgap Semiconductors for Power Electronics
- Materials for Harsh Service Conditions
- Advanced Materials Manufacturing
- Additive Manufacturing
- Composite Manufacturing

Emerging and Crosscutting Areas

- Clean Water
- Energy-Efficient Advanced Computing
- Motor-Driven Systems
- Technology Partnerships
- Workforce Development
- Communications and Outreach
Roll to Roll Advanced Materials Manufacturing Multi-Lab/Industry Collaboration

- **Goals depending on technology area:**
  - Increase throughput by 5x and reduce production footprint
  - Reduce energy consumption by 2x
  - Increase production yield by 2x
  - Enable substantial shift of manufacturing to the United States by assisting in the development of a domestic supply chain
Lab/Industry Partnership Started with ORNL & Kodak 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
Key Applications for Investment by DOE

- Membranes
  - Chemical separation
  - Water purification
  - Water desalination
- Flexible devices
  - Batteries
  - Fuel cells
  - Photovoltaics
  - Electronic films
  - Window films
Outline

• Overview of R2R Collaboration Between National Labs and Industry

• R2R Coating of Thick Structured Electrodes for High-Energy-Density Li-Ion Batteries
  • Conclusions/Future Work

• Single-Process R2R Coating of Gas Diffusion Electrodes for Polymer Electrolyte Fuel Cells
  • Conclusions/Future Work
Thick Electrodes Can Reduce Cost and Increase Energy Density

Advantages of Thick Electrodes:
- Reduces inactive cell components:
  - Cheaper
  - Higher energy density

Cell contains several inactive components (current collector & separator layers)
- Multiplied when cells are stacked to increase capacity
Mass Transport Can Be Difficult in Thick Electrodes

- Mass transport becomes limiting (particularly at high discharge rates)
- Difficult for Li⁺ to diffuse through the entirety of the electrode layer
- **How can we help Li⁺ transport?**
Structured Electrodes Can Facilitate Mass Transport

- Structuring the electrode can help with transport limitations
  - Controlled porosity gradients and pore size distributions

- **Goal:** Use two active material particle sizes to create different thick electrode architectures for improved mass transport and electrochemical performance at high discharge rates

**SmallParticles**

- **NMC 532**
- **Graphite**

- **Higher surface area to volume ratio:**
  - More of the active material is easily accessible for the Li⁺ ions
  - May have higher tortuosity that could hinder Li⁺ diffusion

**LargeParticles**

- **NMC 532**
- **Graphite**

- **Lower surface area to volume ratio:**
  - Less of the active material is easily accessible for the Li⁺ ions
  - May have lower tortuosity that could help Li⁺ diffusion
Thick Structured Electrode Designs for Improved Electrochemical Performance

### Experimental Design:
- Made single-layer (165 mAh) pouch cells with each cathode/anode combination (5 x 5 matrix = 25 total combinations)
- Tested rate performance
  - C/5 Charge, Varied Discharge Rates from C/10 to 10C

#### Areal Loading & Particle Sizes:
- **Cathode** (NMC 532):
  - 25 mg/cm²
  - ~6 & 12 µm Particles
- **Anode** (Graphite):
  - 15 mg/cm²
  - ~10 & 20 µm Particles

**Mixed Two-Layer:**
- Small on Bottom/Large on Top

**Two-Layer:**
- Large Bottom/Small Top

**Two-Layer:**
- Small Bottom/Large Top

**SEM images courtesy of ANL**
Particle Size Makes a Significant Difference in Rate Performance

For High Discharge Rates (2C and 3C):
- Changing the cathode particle size improves the capacity retention by \(~2X\) (~25% to 55%)
  - *Small particle size is better*—probably more difficult for Li\(^+\) to diffuse through entirety of large particles
- Using a *large* particle anode improves capacity retention when paired with a small particle cathode but makes no difference when paired with a large particle cathode
Structured Electrodes Further Improve High-Rate Performance

- Structuring the cathode and anode further improves capacity retention at 2C (to 59%)
- Best performing combination: Two-layer cathode with large particles near the current collector and two-layer anode with small particles near the current collector

![Graph showing rate performance comparison for all anode/cathode combinations. The graph compares the percentage of original capacity against C rate. The best cathode/anode pair consists of a two-layer cathode with large particles near the current collector and a two-layer anode with small particles near the current collector. The worst pair consists of a single-layer cathode and an anode with small particles near the current collector. ](chart.png)
Cathodes Show Clear Performance Trend

Rate Performance Comparison: Best and Worst Anode/Cathode Combinations

- Cathodes do show a trend:
- **Best performing**: All small particles & two-layer with large particles near the current collector
- **Worst performing**: All large particles & two-layer with small particles near the current collector
Two-Layer Cathodes with Large Particles on Bottom Show Better High-Rate Performance

- Cathodes with large particles near the current collector and smaller particles near the separator perform best at 2C and 3C
- **Choice of anode** clearly also makes a significant difference
Two-Layer Anodes Do Not Show Clear Performance Trend

- Not clear whether large or small particles on bottom of anode is better
- Performance seems to depend much more on which cathode it is paired with
Total Pore Volume and Distribution Also Affect Performance

- For single-layer cathodes:
  - All small particle cathode → highest total pore volume → good rate performance
  - All large particle cathode → lowest total pore volume → bad rate performance

- For two-layer cathodes:
  - Large particles on bottom → lower total pore volume → good rate performance
  - Small particles on bottom → higher total pore volume → bad rate performance

- Distribution and location of pores must also play a role in rate performance
Conclusions/Future Work

- Used different active material particle sizes to make thick structured cathodes (25 mg/cm²) and anodes (15 mg/cm²) in 5 different configurations
- Tested the rate performance of single-layer pouch cells made with 25 structured cathode/structured anode combinations

Both particle size and particle configuration make a significant difference in the capacity retention at high C rates
- 2X improvement at 2C (from 28% to 59%)
- Both the cathode and anode particle size/configuration affect the rate performance
  - Changing the cathode particle size/configuration makes the biggest difference
  - Anode trends are not as clear
- Small particle cathodes perform better than large particle cathodes
- Best overall combination is a two-layer cathode with large particles on the bottom and a two-layer anode with small particles on the bottom
- Mercury porosimetry shows that total pore volume, pore size, and pore size distribution affect performance

Future Work
- Currently performing cycle life testing on a subset of cathode/anode combinations
  - Plan to do post-mortem analysis on these cells
- Can use this information to optimize electrode design for further rate performance improvement
Outline

• Overview of R2R Collaboration Between National Labs and Industry

• R2R Coating of Thick Structured Electrodes for High-Energy-Density Li-Ion Batteries
  • Conclusions/Future Work

• Single-Process R2R Coating of Gas Diffusion Electrodes for Polymer Electrolyte Fuel Cells
  • Conclusions/Future Work
Polymer Electrolyte Fuel Cell Manufacturing Challenges

- Catalyst layer coating has been optimized for lab-scale fabrication, relying on time-intensive processes and multiple steps

- To enable the adoption of fuel cells as a component to the U.S. energy portfolio, catalyst layer coating must be scaled to continuous process

- Current standard manufacturing practice is to fabricate catalyst coated membranes (CCMs):
  1. Coat electrodes onto separate transfer liners and then hot-press onto polymer electrolyte membrane
     - Multiple additional steps and materials
  2. Coat electrodes directly onto the polymer electrolyte membrane
     - Difficult due to membrane swelling during coating

- Gas diffusion electrodes (GDEs) are receiving more interest from industry as a pathway for membrane electrode assemblies (MEAs)
  - Different structure may provide improved performance and lifetime
  - May be easier to fabricate and is compatible with R2R processing
Single-Process R2R Manufacturing of GDEs for Polymer Electrolyte Fuel Cells

**Challenge:** GDEs require an over-layer of ionomer to achieve performance comparable to CCMs

**Goal:** Explore, understand, and optimize material and process parameters for single-process (one-step coating) R2R manufacturing of GDEs with comparable performance to CCMs

**Strategy 1:** Controlled distribution of materials – Design catalyst ink and coating process to promote segregation of the ionomer

**Strategy 2:** Dual slot die coating – Coat catalyst and ionomer inks simultaneously to create an ionomer-rich top surface

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

- Identified solvent influence on catalyst aggregation, ink rheology, and ionomer distribution

Significance and Impact

- Showed that alcohol-rich solvent (red lines) results in more mobile ionomer
- Suggests alcohol and water ratio can be tuned to control ionomer distribution

Scott Mauger/ Mike Ulsh/ Debbie Myers
Studied Higher Boiling Point Alcohols to Control Ionomer Distribution (NREL)

**Achievement**
- Determined which high boiling point alcohols can be used to make good ionomer dispersions

**Significance and Impact**
- Demonstrated which alcohols can be used to create catalyst inks

<table>
<thead>
<tr>
<th>Solvent</th>
<th>24 hrs</th>
<th>72 hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O/1-PA</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>H2O/2-PA</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>NMP</td>
<td>✗</td>
<td>✔</td>
</tr>
<tr>
<td>DMF</td>
<td>✔</td>
<td>✔</td>
</tr>
<tr>
<td>DMF/H2O</td>
<td>✗</td>
<td>✗</td>
</tr>
</tbody>
</table>
MEAs Can be Fabricated Using High Boiling Point Alcohol (NREL)

**Achievement**
- Fabricated GDEs with 1,2-pentanediol to control ionomer distribution

**Significance and Impact**
- Showed higher boiling point alcohols can be used to make electrodes that match those made with lower boiling point alcohols

1-Propanol
Boiling point: 97 °C

\[
\text{H}_3\text{C} - \text{OH}
\]

1,2-pentanediol
Boiling point: 209°C

\[
\text{H}_3\text{C} - \text{OH} \quad \text{H}_3\text{C} - \text{OH}
\]
Achievement
- Showed GDEs made with smoother microporous layer produce higher performance MEAs

Significance and Impact
- Significantly reduced ionomer needed to achieve baseline mass activity
- This will likely be better for oxygen mass transport
In Situ USAXS Analysis

Achievement
- Correlated USAXS measurements of catalyst ink particle size with fuel cell performance

Significance and Impact
- Water-rich solvent produces more dispersed ink
- Water-rich solvent results in better high-current density performance
- Improved high current-density performance due to lower non-Fickian Resistance ($R_{NF}$) for oxygen transport measured in limiting current measurements
Conclusions/Future Work

- Investigated effect of several different parameters on catalyst ink rheology for single-process R2R coating of GDE with ionomer-rich surface layer:
  - Solvent influences ink rheology and catalyst layer microstructure
  - Alcohol/water ratio can be tuned to control ionomer distribution
    - High boiling point alcohol can be used
  - Water-rich solvent produces more dispersed ink & better high-current density performance

Future Work
- Further tune alcohol/water ratio
- Explore different alcohols and drying temperatures
- Slot-die coatings of GDEs based on optimized catalyst ink formulations
- Dual slot-die coatings of GDEs with ionomer and catalyst layers coated simultaneously
Acknowledgments

- U.S. DOE Office of Energy Efficiency and Renewable Energy (EERE) Advanced Manufacturing Office (Program Manager: Dave Hardy)

Oak Ridge National Laboratory
- Jianlin Li
- David L. Wood III
- Claus Daniel
- Marissa Wood

Argonne National Laboratory
- Bryant J. Polzin
- Andrew Jansen
- Alison R. Dunlop
- Gregory K. Krumdick
- Yupo Lin
- Debbie Myers
- Jae Hyung Park
- Venkat Srinivasan

National Renewable Energy Laboratory
- Mike Ulsh
- Scott Mauger
- Bertrand Tremolet de Villers

Lawrence Berkeley National Laboratory
- Vince Battaglia
- Kenny Higa
- Gerd Ceder
- Olga Kononova
- Marca Doeff
- Eongyu Li