Influence of Ink Formulation and Drying Conditions on Ionomer Distribution in High-Performance Roll-to-Roll-Coated Gas-Diffusion Electrodes

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Roll-to-Roll Manufacturing

**Electrocatalyst approaches and challenges for automotive fuel cells**

Mark K. Debe

10% of 2030 market = 15M vehicles/year
= 4.5B MEAs/year

- 20 production lines – 585 MEAs/min
- Coating – 1 m wide x 20 m/min

**High-performance R2R-manufactured MEAs needed to meet cost and volume targets**
Direct Coating vs Decal Transfer

**Decal Transfer**
- Catalyst Ink
- PTFE
- Coat and Dry
- Hot Press
- Membrane
- Peal
- Membrane or GDM
- Coat and Dry

**Direct Coating**
- Coat and Dry
Motivation for Direct Coating

<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)</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>
</tbody>
</table>

- Direct coating offers significant savings over decal coating
- Gas diffusion media easier to coat on than membrane

Data courtesy of Strategic Analysis, Inc.
The GDE Challenge

- Spray-coated GDEs often don’t perform as well as CCMs
- Need an ionomer overlayer to form good GDE-membrane interface

Two coating steps (CL + overlayer) does not have an advantage over decal process

The Roll-to-Roll Advantage

- In colloidal mixtures materials can phase separate form enriched surfaces

- Separation is favorable when:
  - Evaporation >> Diffusion, Sedimentation
  - Large difference in particle size
  - Higher concentration of small particles

- Goal—can we design an ink and single coating step that leads a GDE with an ionomer rich surface

Small Scale Coating Trials

- Mayer Rod coating on SGL 29BC diffusion media to simulate R2R coating
- Increase drying temperature to increase evaporation rate
  - 25, 60, and 80 °C
- Increase ionomer:carbon ratio to increase volume of ionomer available to move to surface
  - 0.9, 1.2, 1.6 I/C
- Ink
  - Pt/HSC (TKK TEC10E50E): 3.2 wt%
  - Dispersion Media: water/1-propanol (75/25 w/w)
  - Nafion, 1000 EW
**Measurement of Surface Ionomer**

### Kelvin Probe Method

- Ambient
- Non-contact
- Non-destructive
- Relative measurement

### X-ray Photoelectron Spectroscopy

#### C 1s

- **Ionomer**
- **Pt/HSC**

#### Coating Method Table

<table>
<thead>
<tr>
<th>Coating Method</th>
<th>I/C</th>
<th>C/I Cc</th>
<th>ΔCPD [mV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spray-coated without overlayer</td>
<td>0.9</td>
<td>0.21</td>
<td>-</td>
</tr>
<tr>
<td>Spray-coated with overlayer</td>
<td>0.9</td>
<td>0.38</td>
<td>1104</td>
</tr>
<tr>
<td>Mayer Rod</td>
<td>0.9</td>
<td>0.49</td>
<td>605</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>0.58</td>
<td>726</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>0.86</td>
<td>933</td>
</tr>
</tbody>
</table>

Increasing I/C and drying temp increase surface ionomer content
Increasing I/C:
• Increases conductivity
• Decrease diffusivity
Slot-Die-Coated GDEs

- Same ink as rod coating
- Coating speed - 1 m/min
- Dry at 80 °C
- Freudenberg H23C8 diffusion media

### X-ray Photoelectron Spectroscopy

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<td>0.21</td>
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<tr>
<td>Spray – overlayer</td>
<td>0.9</td>
<td>0.38</td>
</tr>
<tr>
<td>R2R slot die</td>
<td>0.9</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>3.6</td>
</tr>
</tbody>
</table>

*R2R GDEs show same trends as rod coated*
Fuel Cell Performance

- **1-step R2R GDEs perform as well as 2-step spray-coated GDEs**
- High performance also shown with PtCo-based R2R GDEs

![Graph 1](image1.png)

0.1 mg_{Pt}/cm^2
100 %RH
80 °C
150 kPa_{Abs}

![Graph 2](image2.png)

R2R GDEs
0.9 I/C
H₂/N₂ Impedance Spectroscopy

\[ Z(\omega)_{\text{model}} = j\omega L_{\text{wire}} + R_\Omega + \sqrt{\frac{R_{\text{CL}}}{Q_{\text{DL}}(j\omega)\phi}} \coth\left(\sqrt{\frac{R_{\text{CL}}}{Q_{\text{DL}}(j\omega)\phi}}\right) \]

Setzler & Fuller, JES, 162 (6) F519-F530 (2015)
https://github.com/NREL/OSIF

100 %RH
0.2/0.2 sccm H₂/N₂
80 °C
\(V_{\text{DC}} = 200 \text{ mV}\)
\(V_{\text{AC}} = 1 \text{ mV}\)
1 – 10 kHz

Coating Method

<table>
<thead>
<tr>
<th>I/C</th>
<th>( R_{\text{CL}} ) [mΩ-cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>92 ± 10</td>
</tr>
<tr>
<td>1.2</td>
<td>88 ± 10</td>
</tr>
<tr>
<td>1.6</td>
<td>81 ± 10</td>
</tr>
</tbody>
</table>

Spray – without ionomer overlayer
0.9 222 ± 10

Spray – with ionomer overlayer
0.9 108 ± 10

0.9 I/C has sufficient ionomer to form good interface with membrane
• Increasing drying temperature leads to ionomer enrichment at GDE surface
• Ionomer rich surface forms low resistance interface with membrane
• 1-coating step R2R GDEs have same performance as 2-step spray coated GDEs
• GDEs are viable for industrial manufacturing
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