Novel ionomers and electrode structures for improved PEMFC electrode performance at low PGM loadings

DoE Annual Merit Review
Washington, DC, April 30, 2019

Project FC155: PI: Andrew Haug, 3M
BUDGET & Status

Timeline
- Project start date: 10/1/16
- Project end date: 9/30/19
  - 29 of 36 months complete @ AMR

Budget
- Total Project Budget: $3,245,349
  - Total Recipient Share: $649,071
  - Total Federal Share: $2,596,278
- Total Project Costs:* $2,148,352
  - Current Recipient Share: $428,089
  - Current DOE Share: $1,712,356
* As of 1/31/19
** Sub expenses as of 1/1/19
  Running roughly 3 months underspent

Barriers addressed
- Cost, durability, performance
- Operational robustness

Partners
- SUBCONTRACTORS
  - Michigan Technological University
  - Tufts University
  - FCPAD:
    - LBNL, ORNL, NREL, LANL, ANL
- PROJECT LEAD:
  - 3M
Key Barrier: Cathode Transport limitations

Dispersed Cathodes at SEF’s below $100 \text{ cm}^2_{\text{PGM/cm}^2_{\text{planar}}}$
- Transport losses become significant

Traditional NSTF cathodes break this trend
- SEF’s as low as 10.

Likely that *oxygen transport through ionomer* near the reaction site is a key limitation

**FC155 goal is to**
- Understand and improve Ionomer, bulk & local electrode transport
- Integrate NSTF into a dispersed electrode
- Maintain NSTF activity and durability
- Achieve high performance and robustness

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IMPROVED IONOMER

2 methods to improve transport

Dispersed NSTF

Incorporate NSTF into powdered electrode

- 10-100X thicker than NSTF
- Contains ionomer
- Improved operational robustness
- Not constrained to planar NSTF loadings

Approach

10 micron

COMBINE
## Relevance, Objectives & Status

<table>
<thead>
<tr>
<th>METRIC</th>
<th>2020&lt;sup&gt;1&lt;/sup&gt; Target</th>
<th>FC155 Target</th>
<th>3/2017</th>
<th>3/2018</th>
<th>2/2019</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGM total loading, mg/cm&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.125</td>
<td>0.125</td>
<td>0.102&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.102&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.095&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>PGM total loading, g / kW [150 kPa abs]</td>
<td>NSTF Ionomer 0.125</td>
<td>0.125</td>
<td>0.172&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.172&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.172&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>Mass activity @ 900 mV iR-free, A/mg</td>
<td>NSTF Ionomer 0.44</td>
<td>0.44+</td>
<td>0.28+</td>
<td>0.28+</td>
<td>0.31</td>
</tr>
<tr>
<td>Support AST, % mass activity loss, 5k cycles</td>
<td>NSTF Ionomer &lt; 30</td>
<td>&lt; 30</td>
<td>28% (Pt)</td>
<td>&lt;10% (Pt)</td>
<td>&lt;10% (Pt)</td>
</tr>
<tr>
<td>Electro catalyst AST, mV loss @ 0.8 A/cm&lt;sup&gt;2&lt;/sup&gt;</td>
<td>NSTF Ionomer &lt; 30</td>
<td>&lt; 30</td>
<td>NA</td>
<td>80&lt;sup&gt;5&lt;/sup&gt;</td>
<td>80&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td>Electro catalyst AST, % Mass activity loss</td>
<td>NSTF Ionomer &lt; 40</td>
<td>&lt; 40</td>
<td>45% (Pt)</td>
<td>40% (Pt)</td>
<td>41% (Pt/Ir)</td>
</tr>
<tr>
<td>MEA Robustness (cold/ hot / cold transient)</td>
<td>NSTF Ionomer 0.7/0.7/0.7</td>
<td>&gt;0.7/0.7/0.7</td>
<td>0.83/0.79/1.0</td>
<td>0.93/0.84/0.90</td>
<td>0.93/0.84/0.90</td>
</tr>
<tr>
<td>Ionomer Conductivity (S/cm, 80C, 50%RH)</td>
<td>---</td>
<td>0.087</td>
<td>0.050</td>
<td>0.070</td>
<td>0.099</td>
</tr>
<tr>
<td>Ionomer Bulk O&lt;sub&gt;2&lt;/sub&gt;, perm (mol·cm&lt;sup&gt;-1&lt;/sup&gt;·cm&lt;sup&gt;-2&lt;/sup&gt;·kPa&lt;sup&gt;-1&lt;/sup&gt;), 80C, 50RH</td>
<td>---</td>
<td>1.8E-13</td>
<td>2.0E-13</td>
<td>2.3E-13</td>
<td>2.1E-13</td>
</tr>
</tbody>
</table>

<sup>1</sup> All metrics and DOE 2020 targets are taken from DE-FOA-0001412
<sup>2</sup> 0.025 mgPt/cm<sup>2</sup> anode
<sup>3</sup> 3M transient protocols used for NSTF testing

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4 At 0.661V for 80/68/68C, 7.5 psig, 0.686V for 90/84/84C, 21/6 psig
5 At 70/70/70C, 0 psig
Collaboration & Coordination

INTEGRATE to Cathode

Ionomers
- Membranes
- Thin films
- Electrodes
- CCMs

NSTF [POWDER]
- Electrodes
- CCMs

MTU
- Washburn
- Hele Shaw, AFM
- AFM, PNM model
- STEM

TUFTS
- nanoCT
- Electr. Cond.
- InoperandoCT
- Electrode Cond.

FCPAD
- GISAXS, WAXS
- SEM, STEM
- AST testing, RDE
- Water uptake
- Conductivity

3M
- O₂ perm
- Perf Testing
- AST testing
**Progress and Objectives**

### Milestone Summary Table

<table>
<thead>
<tr>
<th>BP1</th>
<th>Go/NoGo: NSTF electrode ECSA &gt;= 15 m²/g, 40 cm²/cm², 0.7 robustness. Ionomer bulk O2 perm + conductivity &gt; 3M825 baseline</th>
<th>Q/M</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>TASK</td>
<td>Synthesize IMIDE#1, Make 20+ grams of NSTF 25 ugPt/cm2 powder.</td>
<td>1/3</td>
<td>100</td>
</tr>
<tr>
<td>TASK</td>
<td>Validate DoE AST tests, specialty tests, run baseline with 3 ICs, 3 loadings..</td>
<td>2/6</td>
<td>100</td>
</tr>
<tr>
<td>TASK</td>
<td>Characterize ionomer, Pt/C, and powder NSTF (SEM, TEM, NanoCT, etc)</td>
<td>3/9</td>
<td>100</td>
</tr>
<tr>
<td>TASK</td>
<td>NSTF powder electrode &gt;= 0.30 A/mg Pt, NanoCT disp NSTF,</td>
<td>4/12</td>
<td>100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>BP2</th>
<th>Go/NoGo: Ionomer exceeds 3M825 O₂ perm by 33% with similar or improved conductivity. 0.35 A/mg Pt, 0.175 g/kW power output</th>
<th>Q/M</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>TASK</td>
<td>Reaction-kinetics model added to PNM framework. PNM predicts pol curves at T = 40 °C and 80°C.</td>
<td>5/15</td>
<td>100</td>
</tr>
<tr>
<td>TASK</td>
<td>NSTF Cathode ECSA &gt;= 25 m²/g.</td>
<td>6/18</td>
<td>100</td>
</tr>
<tr>
<td>TASK</td>
<td>MTU/Tufts: Baseline structures, electrochem input to PNM, delivering initial predictions.</td>
<td>7/21</td>
<td>100</td>
</tr>
<tr>
<td>TASK</td>
<td>NSTF activity &gt;=0.35 A/mg Pt in an electrode. 0.2 g/kW with NSTF containing electrode. *0.31 A/gm_PGM achieved with NSTF, 0.36 A/mg_PGM with durable dispersed alloy</td>
<td>8/24</td>
<td>95*</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>BP3</th>
<th>END: See Targets slide</th>
<th>Q/M</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>TASK</td>
<td>MTU/Tufts: PNM - continuum predicts pol curves for T = 40 and T = 80C within 10%</td>
<td>9/27</td>
<td>80</td>
</tr>
<tr>
<td>TASK</td>
<td>Support AST targets achieved. Metal cycle AST &lt;40% activity loss.</td>
<td>10/30</td>
<td>100</td>
</tr>
<tr>
<td>TASK</td>
<td>Ionomer with 50% greater O₂ permeability and 50% greater H+ conductivity than 3M825</td>
<td>11/33</td>
<td>100</td>
</tr>
<tr>
<td>TASK</td>
<td>&gt;=0.44 A/mg PGM in electrode. Metal AST &lt;=30% activity loss. 0.125 g/kW.</td>
<td>12/36</td>
<td>40</td>
</tr>
</tbody>
</table>
TASK1: Ionomer Development

**Bulk O₂ permeability**
- GM (Zhang ECS 2013) method
- Imide #4 (vs 825): +92%
- Imide #6 (vs 825): +105%
- Imide #8 (vs 825): +64%

**Bulk conductivity**
- 4 point probe
  - IMIDE#4 (vs 825): +22%
  - IMIDE#8 (vs 825): +74%

**2nd Validation of Imide#6**
- Oxtran O₂ transmission
  - (vs 825): +64% [23C, 0%RH]

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**Bulk O₂ Perm, Conductivity**

IMIDE#8

80C, 50%RH Target

Project Target

825EW baseline

Conductivity, S/cm

O2 perm, [mol*cm*s⁻¹*cm⁻²*kPa⁻¹]
**TASK1: Ionomer Structure**

**Ionomer thin films have been evaluated**
- GISAXS, Ellipsometry
- On Pt and Si substrates

**PFIA and MASC thin films have**
- Larger ionomer domain spacing
- Stronger nano-phase separation
- Reduced preferential orientation parallel to Pt, Si
- More swell with Pt vs. Si

**PFSA & IMIDE#2 more oriented on Pt**
- More likely to lay flat on catalyst

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**Domain Spacing**

**IONOMER Thin Films**

**Ellipsometry**

- Si, 50nm
- Pt, 50nm
- Pt, 20nm

**Results suggest** larger free volume and better transport pathways for ionic and gaseous species, which are favorable outcomes for catalyst performance.
**TASK1: Ionomer Conductivity, Uptake**

**Electrode, Tufts/MTU**

**MTU: Water uptake vs. Ionomer**
- All using I/C=0.9, 10V50E
- Water uptake increases for PFIA, MASC

**Tufts evaluating Ionomer conductivity**
- DC Technique using H₂ pump
- PFIA conductivity @ 80%RH: 8,12X [vs 825, 1000EW]
- I_{PFIA}/C=0.4 equivalent to I_{825}/C=0.8

**Tufts evaluating Ionomer tortuosity**
- Compare DC Technique and AC(EIS) techniques
- Ratio results to estimate H⁺ tortuosity vs. RH

**Washburn method: Electrode Water Uptake**

**Vulcan – Ionomer films**

**KEY**
**TASK 1:** Ionomer Local Gas Transport Electrode, NREL/LBNL/3M

**Less ionomer reduces resistance**
- I/C=0.9 to 0.4 reduced resistance 19-33%
- Seen for H₂ & O₂ transport
- dNSTF and Pt/C systems

**Not yet clear differentiation of ionomer type**
- Results similar to PFSA baselines at 3M, NREL
- Testing more now at NREL

**UNUSUAL Behavior with I/C<0.4**
- 825 PFSA shows increase vs. I/C=0.4
- PFIA & MASC2 do not
- Possible agglomeration, catalyst de-activation at <100%RH

### Graphs
- **Transport Resistance** vs. I/C Ratio
- **Interfacial Resistance** vs. I/C Ratio
- **RₙF [s/cm]** vs. I/C Ratio

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**Technical accomplishments**

**NREL, O₂**

**3M, O₂**

**LBNL, H₂**

**NREL, O₂**
**TASK1+3: Ionomer Integration**

*Lower I/C = Higher catalyst activity*
- Low-Mid SA carbons
- Gr2 carbon activity increased 61%
- Consistent with Shinozaki et al (on RDE)

*Near 0.3 A/mgPt with Pt/Vu*

*Pt-alloy/Gr2 = 0.36 A/mgPt*
- BP2 GNG

*Gr3, Gr3a promise higher activity*
- 3000+ support cycles

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**Graphitized Carbon#2, 825EW**

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K. Shinozaki et al. / Journal of Power Sources 325 (2016) 745
**TASK1+2+3: Ionomer Integration**

**Aggregates & Agglomerates influenced by**
- C-type, %M, Ionomer type, I/C ratio
- ANL using USAXS to quantify
- Low I/C & dNSTF electrodes more agglomerated

**PFIA reduces agglomeration**

**Processing can reduce agglomeration**
- & Increase performance at low I/C

<table>
<thead>
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<th>Type 1</th>
<th>vs</th>
<th>Type 2</th>
<th>&gt;400nm Aggl.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-type</td>
<td>HSC</td>
<td>XC72</td>
<td>7X</td>
</tr>
<tr>
<td>%M/C</td>
<td>XC72</td>
<td>10V50E</td>
<td>50X</td>
</tr>
<tr>
<td>I/C</td>
<td>0.4</td>
<td>0.8</td>
<td>3X</td>
</tr>
<tr>
<td>Ionomer</td>
<td>825</td>
<td>PFIA</td>
<td>2X</td>
</tr>
<tr>
<td>Electrode</td>
<td>dNSTF,</td>
<td>10V50E</td>
<td>~75X</td>
</tr>
<tr>
<td></td>
<td>XC72, I/C=0.4</td>
<td>Baseline</td>
<td>(500X for HSC)</td>
</tr>
</tbody>
</table>

**dNSTF electrode HIGHLY agglomerated**
TASK1,3: BEST in CLASS

**CCM Package SPECS:**
- 0.025 mg Pt/cm² anode
- Better membrane, GDL

**Alloy M/Carbon, PFIA, I/C=0.4**
- 0.125 g/kW @ 0.661V [80°C, 7.5 psig]
- 0.125 g/kW @ 0.686V [90°C, 21.6psig]

**Good Pt/C performance at <0.07 mg Pt/cm²**
- Imides shows H₂/Air gains

**Technical accomplishments**
- Conditioning curves, H₂/Air, CF=800/1800 SCCM, T=60/60/60
- 10V50E, 825, IC=0.9, 0.20 mgPt/cm² CA, BASELINE
- 10V50E, PFIA, IC=0.6, 0.11 mgPt/cm² CA
- 10V50E, IMIDE#1, IC=0.9, 0.09 mgPt/cm² CA
- ALLOY, PFIA, IC=0.4, 0.095 mgPt/cm² CA

**Imide conditioning slow**
- Conditioning curves, H₂/Air, CF=800/1800 SCCM, T=60/60/60
- THERMAL CYCLES
- 75/70/70C
- 800/1800 SCCM
- 0.8V
- IMIDES
- 825EW

**Cell Voltage, V**
- 80/68/68C,
  S=2.0/2.5,
  P=7.5 PSIG

**Current Density, A/cm²**
- 0.639
- 0.648
- 0.649
- 0.661
- 0.4
- 0.5
- 0.6
- 0.7
- 0.8
- 0.9
- 1
- 0 0.5 1 1.5 2

**mg Pt/cm² of 10V50E**
- 0.1
- 0.2
- 0.06
- 0.1
- 0.15
- 0.2
- 0.25
- 0.3

**mg Pt/cm² of 10V50E**
- 0.1
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- 0.1
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- 0.2
- 0.25
- 0.3

**Current Density, A/cm²**
- 0.4
- 0.5
- 0.6
- 0.7
- 0.8
- 0.9
- 1
- 0 0.5 1 1.5 2
## TASK1,3: BEST in CLASS

### Initial attempts have combined

- Activity & conductivity gains with
- Support stability
- Metal stability

### Areas of focus/improvement

- Low initial surface area – increase this
- Metal stability
- Optimizing balance of parts

### Technical accomplishments

<table>
<thead>
<tr>
<th>Property</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial activity, A/mgPt</td>
<td>0.31</td>
</tr>
<tr>
<td>Local O₂ resistance, S/cm</td>
<td>-25.9% (vs baseline)</td>
</tr>
<tr>
<td>Electrode ionomer thin film conductivity</td>
<td>8X vs. 825</td>
</tr>
<tr>
<td></td>
<td>12X vs. 1000</td>
</tr>
<tr>
<td>Process Improvement</td>
<td>18% power</td>
</tr>
<tr>
<td></td>
<td>[@0.067 mgPt/cm²]</td>
</tr>
<tr>
<td>Support stability</td>
<td>5000+ cycles</td>
</tr>
<tr>
<td>Metal Stability (will improve with package optimization)</td>
<td>-39.6% ECSA</td>
</tr>
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<td></td>
<td>-69mV (0.8 A/cm²)</td>
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<td>-39mV (0.5 A/cm²)</td>
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**Property**

- Performance

**Initial activity, A/mgPt**: 0.31

**Local O₂ resistance, S/cm**: -25.9% (vs baseline)

**Electrode ionomer thin film conductivity**
- 8X vs. 825
- 12X vs. 1000

**Process Improvement**
- 18% power
  - [@0.067 mgPt/cm²]

**Support stability**: 5000+ cycles

**Metal Stability**
- (will improve with package optimization)
  - -39.6% ECSA
  - -69mV (0.8 A/cm²)
  - -39mV (0.5 A/cm²)

### 3M

- Initial attempts have combined Activity & conductivity gains with Support stability Metal stability
- Areas of focus/improvement Low initial surface area – increase this Metal stability Optimizing balance of parts
TASK 2: Powdered NSTF

**Powdered NSTF**
- Eliminates geometric constraint
- Requires new variables (Wh/C, I/C)

**Task 2 Targets met:** ECSA, SEF

**New materials coming**
- ECSA = 28-30 m²/g at 40°C
- 0.4 A/mgPt with no transmission metals

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**Technical accomplishments**

<table>
<thead>
<tr>
<th>TARGET</th>
<th>Status</th>
<th>Key issue</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECSA = 25 m²/g</td>
<td>Complete</td>
<td></td>
</tr>
<tr>
<td>Surface Roughness</td>
<td>Complete</td>
<td></td>
</tr>
<tr>
<td>Operating range</td>
<td>Complete</td>
<td>Ensure with downselects</td>
</tr>
<tr>
<td>Metal AST – ECSA</td>
<td>Complete</td>
<td></td>
</tr>
<tr>
<td>Support AST</td>
<td>Complete</td>
<td></td>
</tr>
<tr>
<td>Metal AST – 0.8 A/cm²</td>
<td>80 mV</td>
<td>H+ transport</td>
</tr>
<tr>
<td>Activity</td>
<td>0.31</td>
<td>Electrode Structure (Pt/Ir) Transition metal loss (Pt-alloy)</td>
</tr>
</tbody>
</table>
**TASK2: dNSTF, Performance Root Cause**

ANL, LANL, LBNL, NREL, ORNL, MTU, Tufts

**Mid-High current performance loss**

- Lower I/C improves high currents
- Lower Wh/C improves high currents
- PFIA improves @ high currents
- Local O2 transport EXCELLENT
- Agglomeration is SEVERE
- Proton Transport Poor and RH sensitive

Next slides show the above in detail

**ANL work**

<table>
<thead>
<tr>
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<th>&gt;400nm Agglomeration</th>
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</table>

dNSTF electrode HIGHER agglomerated

So much performance loss
Only 15%ECSA loss!!!
**TASK2,3:** dNSTF, Performance Root cause

**Reduced \( \text{O}_2 \) transport resistance**
- More carbon, less ionomer
- I/C=0.8 to 0.4 reduced resistance ~31%
- Wh/C=2.5 to 1 0 reduced resistance ~15%

**Best local transport achieved (NREL)**
- NSTF25Pt, PFIA, I/C=0.4, Wh/C=1.0
- -39.6% vs. Baseline 10V50E
- -61.4% vs. Pt/HSC

**Impedance verifies transport gains**

**Transport Gains = performance gains.**

---

**NREL, \( \text{O}_2 \)**

**GDS Curve**
- 10V50E, 0.11Pt, 825, IS=0.6, WH/S=, SEF=58.8
- NSTF 25Pt, 0.208Pt, 825, IS=0.6, WH/S=1, SEF=45.9
- NSTF 25Pt, 0.245Pt, 825, IS=0.6, WH/S=2.5, SEF=50.5
- NSTF 25Pt, 0.21Pt, 825, IS=0.8, WH/S=1, SEF=40.8

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**LANL**

**H2-Air Impedance**
- 100%RH, 150 kPa, 80C
- 800/1800 sccm
- 5 cm\(^2\) cell

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**NREL, \( \text{O}_2 \)**

**Baseline**

**Lower I/C Lower Wh/C**

**Higher Voltage**

**Voltage Level 0.34 Current Level 10.50 NSTF #2**

**Voltage Level 0.55 Current Level 10.50**

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**3M**

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**Technical accomplishments**
TASK2,3: dNSTF, Performance Root cause

**NREL / LANL /Tufts**

**Evaluating key variables**
- Gas transport resistance: It's Good
- Change with $P_{O_2}$ is small: Not kinetic
- H+ resistance (transmission line): Low & RH sens.
- Performance vs. RH (LANL): RH sensitive

**Impedance in $H_2$/Air**
- Low current densities, NSTF much worse
- High current densities, NSTF much better

**Tufts performed CO stripping**
- Disp. NSTF vs. M/C (10V50E)
- Ionomer coverage of whiskers likely low
  - Due to agglomeration?
  - Contributing to poor conductivity?

**Dispersed NSTF is likely proton transport limited**
TASK4: Tufts-MTU Electrode Transport Model

Cathode/Anode transport fluxes Model between the membrane and the gas channel

Electrode network approach

Calibration & Validation of the coupled model

Investigating impacts of whisker coverage by ionomer

- Impacts what the electrode pores see
- Impacts local conductivity
- Low coverage = more pore flooding

Currently 50% ionomer coverage on all Whiskers

80C, 80%RH, 7.5 psig
I/C=0.9, Wh/C=0.9

Prediction

80C, 80%RH, 7.5 psig
I/C=0.9, Wh/C=0.9
TASK 2:  Best in Class performance

**NSTF 25 ug/cm$^2$ [PLANAR] + PFIA**
- Best performance
- Mostly overcomes resistance loss issue
- Best local transport of any electrode tested (NREL)

**NSTF 28 ug/cm$^2$ [PLANAR] PtNiRu + IMIDE#1**
- 0.31 A/mg$_{PGM}$, highest activity to date

**NSTF 47/12 ug/cm$^2$ [PLANAR] Pt/Ir + IMIDE#1**
- 0.172 g/kW achieved without best in class package
- 78% activity retained in dispersed format
- Best local transport of any electrode tested [3M]
- 18% ECSA loss
- Can readily pass Support AST

**Prediction**

**Achievement**
SELECTED AMR Comments

Overall, project was good on approach and accomplishments

Presentation was weak on collaboration
- Many results came after 5/2018
- Collaborations shed light on many issues

Multiple comments implying 3M is “layering” NSTF to make a cathode
- This work focuses mainly on dispersing, not layering, NSTF

The future work could be more detailed, and durability should be more thoroughly addressed
- Hopefully this presentation corrected this

The link between NSTF and novel electrode ionomers is not clear.
- NSTF catalyst was seen as a means to achieving activity and durability targets

Why MASC and imide-based ionomers was chosen is not clear
- Multi-acid side chain ionomers are more conductive
- Imides offer path to higher O\textsubscript{2} permeability

AMR 2018

Overall Project Score: 3.2 (7 reviews received)

The vertical hash-lines represent the highest and lowest average scores received by projects in the sub-program.
Summary

TASK 1: IONOMER
- **Achieved project targets** (ionomer with >50% oxygen permeability & conductivity vs. 3M825 PFSA)
- Characterized new ionomer thin films, evaluated electrodes, tested CCM for performance, durability
- Showed PFIA 8X more conductive as a thin film vs. 825PFSA, allowing low I/C operation
- Imide ionomers showing mixed gains at low RH H₂/Air operation, minimal at 100% RH or H₂/O₂ operation

TASK 2: DISPERSED NSTF
- Exceptional metal AST shown with Pt/Ir NSTF electrodes but unusual “resistance-like” loss
- Entire team root causing “resistance like” – pointing to protonic conduction issue
- High electrode agglomeration may be contributing to poor whisker coverage by ionomer
- Local gas transport is excellent – lowering I/C and Wh/C raises performance
- Activity of 0.31 A/mgPt achieved

TASK 3: ELECTRODE INTEGRATION
- Low I/C electrodes with PFIA: 18-31% less transport resistance, up to 61% activity gains, improved power
- Achieved 0.36 A/mgPt with Alloy on Graphitized carbon.
- Achieved support stability targets, getting close to metal stability targets
- NSTF transition metals leach out in electrode lowering activity. Pt/Ir active catalyst will be pursued as a result.
  - **Achieved support stability targets, Achieved metal AST ECSA targets (NSTF)**

TASK 4: PNM model development in operation
- Looking into impacts of whisker coverage – and impact on water management.
- Will investigate agglomeration and ionomer properties on water management and performance.
- Look at whisker thermal differences vs. dispersed M/C catalysts.
# Future Work / Key Challenges

## Future Work

### Key Items
- Resolve dispersed NSTF conductivity issue
- Link ionomer O\(_2\) perm to performance gains
- Optimize new ionomers + durable M/C catalysts
- Optimize processing of low I/C systems
- Complete CCM package optimization for best cathode
- Achieve performance + durability targets

## Task 1: Ionomer
- Develop additional ionomer with novel endgroups
- LBNL: Look at super-MASC, IMIDE#6 with GISAXS
- Link bulk membrane oxygen permeability to areas of performance enhancement
- Incorporate more conductive MASC into electrode
- Tufts: Look at imide thin film ionic conduction
- Tufts: CO stripping of low I/C, processed electrodes

## Task 2: Dispersed NSTF
- Continue processing to improve conductivity
- ALL: Investigate “un-agglomerated” disp. NSTF electrodes
- Improve ionomer coverage of NSTF whiskers
- Further optimize NSTF 28/12 Pt/Ir to achieve >0.35 A/mgPt
- Incorporate more active materials
- LANL: Define conductivity trends of disp. NSTF electrodes
- Tufts: CO stripping of “processed” NSTF electrodes

## Task 3: Integration
- ALL: Explore processing impacts on low I/C, MASC materials
- ANL,NREL: Further explore performance vs. agglomeration
- LANL: Low I/C conductivity evaluations for M/C materials
- Continue to incorporate NSTF with new ionomers
- Explore new incorporation methods with NSTF
- Optimize activities of new durable catalysts
- If needed: integrate NSTF & dispersed M/C materials
- Tufts: Ionic tortuosity vs. processing for Low I/C

## Task 4: Modeling
- MTU: Continue to build fidelity
- MTU/TUFTSRoot cause dispersed NSTF performance issue
- Investigate agglomeration on performance
- Integration low I/C data & identify optimal configuration
BACKUP
Task 3: dNSTF and Transition Metal Issue

Ni and Co leach into electrode pre-test
- PtNi Cathode ionomer is completely neutralized
- Co reduces local $O_2$ transport and performance

MITIGATION & Understanding Necessary
- Increase electrode ionomer & IEC
- Acid wash catalyst to remove excess Ni
- TMI operating window (NREL local transport)

Status: 1st Acid Treatments caused activity loss
- Similar result happen in ink with ionomer (acid)
- Shift focus more to non-transition metal catalysts (Pt/Ir)
- Work on heat treated NSTF for alloy retention

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>State</th>
<th>% Transition Metal Retained</th>
</tr>
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<tbody>
<tr>
<td>PtCoMn</td>
<td>Powder</td>
<td>100 (Co)</td>
</tr>
<tr>
<td></td>
<td>CCM/Untested</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>Tested</td>
<td>20</td>
</tr>
<tr>
<td>PtNi</td>
<td>Powder</td>
<td>100 (Ni)</td>
</tr>
<tr>
<td></td>
<td>CCM/Untested</td>
<td>72.5</td>
</tr>
<tr>
<td></td>
<td>Tested</td>
<td>64</td>
</tr>
</tbody>
</table>

EXCESS Transition metal vs. CA IEC
**TASK 1,3: Electrode Integration for M/C catalysts**

**Additional Metal AST Work**

**OPTIMIZING Durable Carbons**

- I/C and IEC vs. durability
- **Lowering IEC increases durability**
- Tested from 620 to 1200 EW
- End of life performance significantly improved
- Lower I/C limit where high currents suffer

**Graphitized carbon choice** makes a significant difference in metal stability

---

**Technical accomplishments**
**CO displacement Technique**

- **Developed by Feliu:**
  - Constant potential is applied and zero-charge CO displaces adsorbing species on Pt. Oxidative or reductive current can be measured, depends on what type of species are displaced:
    
    \[
    Pt - Ca + CO \rightarrow Pt - CO + Ca^+ + e^- \\
    Pt - An + CO + e^- \rightarrow Pt - CO + An^-
    \]

- Measured displacement current densities are integrated. CO-adsorption takes place without change in oxidation state. We can then calculate the coverage using qstrip.

\[
q_{dis} = q_f - q_i \approx -q_i \\
\theta_{dis} = \frac{2 \times q_{dis}}{q_{strip}}
\]

**AC+DC electrode Technique**

- **DC Technique**
  - Easy to interpret data
  - Contact resistance and membrane resistance isolated
  - Protons pumped through membrane and PCL
  - **Method captures ionomer tortuosity**

- **AC technique**
  - Does not capture layer tortuosity
  - Double layer capacitive charging since no Pt present
  - Capacitive charging only at PEM/electrode interface

---

TASK1: Novel Ionomer Development

Ex-Situ vs. In-Situ

Imide-based materials show gains
- At H\textsubscript{2}/Air, sub-saturated, high stoic
- Bulk O\textsubscript{2} perm also better drier
- Imides #1, 2, 3, 6 tested

Imide not showing H\textsubscript{2}/O\textsubscript{2} activity gains

Results unlike 1200EW PFSA
- Shows H\textsubscript{2}/O\textsubscript{2} activity gains

<table>
<thead>
<tr>
<th></th>
<th>BULK FILM</th>
<th>Local O\textsubscript{2} Transport</th>
<th>Thin film Conductivity</th>
<th>In-cell Tests</th>
<th>Activity</th>
<th>dNSTF</th>
<th>Metal Stability</th>
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<tbody>
<tr>
<td>PFIA &amp; MASC</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
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<td>IMIDES</td>
<td>YES</td>
<td>No, possibly low RH</td>
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<td>H2/Air, &lt;100% RH</td>
<td>Variable</td>
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<tr>
<td>Low I/C</td>
<td>---</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
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<tr>
<td>PFIA + Low I/C</td>
<td>---</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
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</tr>
</tbody>
</table>

Focus is on Low surface area, durable carbons. Metal is on the surface & better interact with ionomer.
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