Highly Active, Durable, and Ultra-low PGM NSTF Thin Film ORR Catalysts and Supports

Overview to DOE Catalysis Working Group
Argonne National Laboratory
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# Project Objective and Relevance

## Overall Project Objective
Develop \textit{thin film} ORR electrocatalysts on 3M Nanostructured Thin Film (NSTF) supports which exceed all DOE 2020 electrocatalyst cost, performance, and durability targets.

## Project Relevance
ORR catalyst activity, cost, and durability are key commercialization barriers for PEMFCs.

3M NSTF ORR catalysts are one leading approach which approach many DOE 2020 targets \textit{in state-of-the-art MEAs}.

Project electrocatalysts will be:
- compatible with scalable, low-cost fabrication processes.
- integrated into advanced electrodes and MEAs which address traditional NSTF challenges: operational robustness, contaminant sensitivity, and break-in conditioning.

## Overall Approach
Establish relationships between electrocatalyst functional response (activity, durability), physical properties (bulk and surface structure and composition), and fabrication processes (deposition, annealing, dealloying) via systematic investigation.

Utilize high throughput material fabrication and characterization, electrocatalyst modeling, and advanced physical characterization to guide and accelerate development.
## Status Against DOE 2020 and Project Targets

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>2020 Target and Units</th>
<th>Project Target</th>
<th>2016 Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum group metal (PGM) total content (both electrodes)</td>
<td>0.125 g/kW</td>
<td>0.1 (0.70V)</td>
<td>0.16&lt;sup&gt;1&lt;/sup&gt; 0.18&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>PGM total loading (both electrodes)</td>
<td>0.125 mg/cm&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.10</td>
<td>0.105&lt;sup&gt;1&lt;/sup&gt; 0.127&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>Loss in catalytic (mass) activity</td>
<td>40 %</td>
<td>20</td>
<td>42&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Loss in performance at 0.8 A/cm&lt;sup&gt;2&lt;/sup&gt;</td>
<td>30 mV</td>
<td>20</td>
<td>-8&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Loss in performance at 1.5 A/cm&lt;sup&gt;2&lt;/sup&gt;</td>
<td>30 mV</td>
<td>20</td>
<td>-68&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Mass activity @ 900 mV&lt;sub&gt;iR-free&lt;/sub&gt;</td>
<td>0.44 A/mg (MEA)</td>
<td>0.80</td>
<td>0.28&lt;sup&gt;3&lt;/sup&gt; (NPTF “M”) 0.47&lt;sup&gt;4&lt;/sup&gt; (NPTF) 0.39&lt;sup&gt;5&lt;/sup&gt; (UTF)</td>
</tr>
</tbody>
</table>

1.015mg<sub>Pt</sub>/cm<sup>2</sup> NSTF anode, 0.075 dealloyed PtNi/NSTF cathode, 0.015 mg<sub>Pt</sub>/cm<sup>2</sup> cathode interlayer.

2.0.02mg<sub>Pt</sub>/cm<sup>2</sup> NSTF anode, 0.091mg<sub>PGM</sub>/cm<sup>2</sup> NPTF “M” cathode, 0.016 mg<sub>Pt</sub>/cm<sup>2</sup> cathode interlayer.

3.NPTF “M” cathode, 0.109mg<sub>PGM</sub>/cm<sup>2</sup> after 30k Electrocatalyst AST cycles.

4.Annealed NPTF P4A Pt<sub>3</sub>Ni<sub>7</sub>/NSTF, 0.12mg<sub>Pt</sub>/cm<sup>2</sup>; adjusted from 0.900V<sub>MEAS</sub> (70mV/dec)

5.Best UTF “A”, 0.027mg<sub>PGM</sub>/cm<sup>2</sup>. Average of two MEAs.
### Approach – Two Distinct Thin Film Electrocatalyst Morphologies

#### Nanoporous Thin Film (NPTF)

<table>
<thead>
<tr>
<th>MEA Conditioning State</th>
<th>Before</th>
<th>After (Dealloyed)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><img src="image1" alt="Before" /></td>
<td><img src="image2" alt="After" /></td>
</tr>
</tbody>
</table>

**NPTF Approach:**

1. Structure/composition/process space optimization to maximize area and minimize leachable TM.
2. Proprietary stabilization approaches to minimize coarsening and TM dissolution.

<table>
<thead>
<tr>
<th>NPTF PtNi/NSTF, “P4A, TFA”</th>
<th>Status</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Activity (A/mg)</td>
<td>0.47</td>
<td>0.80</td>
</tr>
<tr>
<td>Specific Area (m²/g)</td>
<td>19</td>
<td>30</td>
</tr>
<tr>
<td>Spec. Activity (mA/cm²Pt)</td>
<td>2.5</td>
<td>2.6</td>
</tr>
</tbody>
</table>

#### Ultrathin Film (UTF)

<table>
<thead>
<tr>
<th>MEA Conditioning State</th>
<th>Before</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><img src="image3" alt="Before" /></td>
<td><img src="image4" alt="After" /></td>
</tr>
</tbody>
</table>

**UTF Approach:**

1. Structure/composition/process space optimization to develop highly active, stable, and thin surface facets.
2. Maximize NSTF support surface area.

<table>
<thead>
<tr>
<th>UTF “A”/NSTF, Proprietary Process</th>
<th>Status</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Activity (A/mg)</td>
<td>0.39</td>
<td>0.80</td>
</tr>
<tr>
<td>Specific Area (m²/g)</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>Spec. Activity (mA/cm²Pt)</td>
<td>2.5</td>
<td>4.0</td>
</tr>
</tbody>
</table>

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UTF Electro catalysts

UTF “A” Electro catalyst MEA Mass Activity

- “A”: First single alloy system
- Initial work - systematic study of composition, structure, and fabrication process levels.
- Mass activity largely monotonic function of key variables.
- To date, best MEA mass activity approaches 0.39A/mg, ~4x higher than Pt/NSTF.
- Characterization by TEM, EDS, EELS, XAFS in progress. Correlations developing.
- Durability evaluation initiated.

UTF H₂/Air Performance

- UTF performance >> Pt
- High J performance suppressed v. typical higher loadings
- High J performance dictated by absolute cathode surface area
- UTF TGT: >20m²/g, 0.075mg/cm²

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Challenges w/ FC Measurements at Ultralow PGM

- At ultra-low PGM, CV curvature (HER?) makes MEA $H_{UPD}$ integration values questionable.
- New method developed which greatly improves S:N of ECSA as determined by $H_{UPD}$
- ECSA values calculated with same integration limits with both methods.
- CO stripping may be an alternative; have not evaluated.

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Impact of “M” Integration Method on NPTF PtNi Activity, Performance

- Four different “M” integration methods, with several variations within each method.
- Mass activity and H₂/Air performance @ 1A/cm² depend strongly on integration method and level.
- To date, method “D” yielding best combination of BOL activity and performance.
"M" Integration (Type D) Electrocatalyst AST

- With one “M” integration method, conducted Electrocatalyst AST vs. “M” content
- With no “M” (0), > 60% mass activity loss and >40mV loss at 1A/cm² after AST
- With “M”, close to target durability attained and performance for J >0.8A/cm² improved.

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**Approach - Electrocatalyst Simulation**

1. Atomistic determination of catalyst surface structures
   - DFT: Surface energy calculations of Pt skins on Pt alloys

2. Activity predictions of optimized surface structures
   - DFT: Descriptor binding energies on optimized surface structures

3. Model Validation
   - Electrocatalyst Fabrication
     - PVD Deposition
     - Proprietary dealloying and annealing processing
   - Activity Characterization
     - MEA
     - RDE
     - Flow cell
   - Structure/Composition Characterization
     - HAADF-STEM
     - STEM+EDS
     - XAFS / $\Delta\mu$-XANES
     - WAXS
     - XRD
     - XRF
     - HT Methods When Validated

4. Characterization Feedback for Model Refinement

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Purdue has initiated DFT analysis of the stability and activity of UTF “A” catalysts vs. composition and Pt skin thickness.

Large surface stresses can develop if substantially strained; depends on Pt skin thickness.

Activity also depends on surface strain and skin thickness ~ up to 20x higher than Pt predicted.

Model will be tuned based on extensive UTF “A” electrochemical and physical characterization. If validated, will be used for property predictions in new systems.
Electrocatalyst Simulation – KMC of NPTF PtNi

• Johns Hopkins has initiated Kinetic Monte Carlo modeling of composition and structure (surface area) evolution of PtNi during electrochemical dealloying (oxidation/reduction cycles).

• Preliminary model results qualitatively consistent with experiment:
  • Similar sigmoidal composition evolution, slope in transition region, and final composition

• Model will be tuned based on extensive NPTF PtNi dataset. If validated, will be used for property predictions in new systems.

Comparison of composition evolution of experimental NSTF catalyst to simulated average composition of a ~20nm Pt binary alloy sphere as a function of oxidation/reduction cycle number.
- (silver) Pt;
- (red) oxidized Pt;
- (green) Ni.
<table>
<thead>
<tr>
<th>HT Electrocatalyst Fabrication</th>
<th>HT Electrochem. Characterization</th>
<th>HT Physical Characterization</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Deposition</strong></td>
<td><strong>Segmented fuel cell</strong></td>
<td><strong>XRF (comp.)</strong></td>
</tr>
<tr>
<td>• Physical vapor deposition</td>
<td>• Uses effectively same hardware as standard 50cm² test cell</td>
<td>• 1mm resolution</td>
</tr>
<tr>
<td>with appropriate masks.</td>
<td>• Allows evaluation after standard testing (conditioning, ASTs) with no translation (ideally).</td>
<td></td>
</tr>
<tr>
<td><strong>Dealloying – TBD</strong></td>
<td><strong>Multi-channel flow cells – TBD</strong></td>
<td><strong>XRD/WAXS (struct.)</strong></td>
</tr>
<tr>
<td>• Use multi-channel flow cell which incorporates NSTF catalyst on growth substrate</td>
<td>• Surface area, ORR activity determination.</td>
<td>• WAXS at ANL APS demonstrated</td>
</tr>
<tr>
<td>• Use multi-channel potentiostat to independently dealloy each segment.</td>
<td>• On growth substrate (JHU/3M) and with catalyst powder (ANL).</td>
<td>• XRD via benchtop/lab instruments in development at ANL.</td>
</tr>
<tr>
<td>• To be developed at JHU.</td>
<td></td>
<td><strong>XAFS – TBD</strong></td>
</tr>
<tr>
<td><strong>Annealing – TBD</strong></td>
<td></td>
<td>• Project will evaluate possibility of in-operando XAFS of gradient electrocatalysts (ANL)</td>
</tr>
<tr>
<td>• Proprietary 3M process.</td>
<td></td>
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</tbody>
</table>

**Significant first year effort to develop and validate HT fabrication and characterization methods.**

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• Analysis of three replicate annealed PtNi gradient catalysts shows good agreement in lattice constant.
• One trial showed erroneous results over mid-section – cause TBD.
• Lattice constant decreases as Pt mole fraction decreases, as expected.
• Analysis for grain size of this series in progress.
Task 3 - Combinatorial Electrocatalyst Fabrication and Characterization Development – Segmented ECSA

- Pure Pt, loading gradient (20-50µg/cm²), bottom to top.
- Very low roughness factors of ~1-2 cm² Pt/cm² planar required significant method development (software!)
- Detected roughness factor agrees well between segmented cell and homogenous cell.
- Some challenges with reliability of cell setup. Debugging in progress.
Summary

- **UTF and NPTF stabilization approaches are promising**
  - UTF “A”: Up to 0.39A/mg, in MEA (ca. 4x Pt/NSTF). Significant sensitivities to composition, structure, processing. Durability assessments initiated.

- **Electrocatalyst Simulation**
  - DFT
    - Simulations of first Pt alloy system with varying subsurface compositions and Pt skin thicknesses revealing key trends in both stability and activity.
    - Correlations to project experimental data in progress.
  - kMC
    - Initial Pt$_x$Ni$_{1-x}$ surface area and composition evolution simulations agree reasonably well with experiment

- **HT Development**
  - HT electrocatalyst fabrication and composition and structural characterization methods validated.
  - HT electrochemical characterization development in progress. Showing good promise.