Tailored High Performance Low-PGM Alloy Cathode Catalysts

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Materials Science Division
Argonne National Laboratory

Project ID#
FC140

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Timeline
• Project start: 10/2015
• Project end: 10/2018

Budget
• Total Project funding $3.6M
• Funding for FY17: $1.2M

Overview

Barriers to be addressed

1) Durability of fuel cell stack (<40% activity loss)
2) Cost (total loading of PGM 0.125 mg$_{\text{PGM}}$/cm$^2$)
3) Performance (mass activity @ 0.9V 0.44 A/mg$_{\text{Pt}}$)

Partners:
• Argonne National Laboratory – MERF - CSE – Greg Krumdick, Debbie Myers
• Lawrence Berkeley National Laboratory – Peidong Yang
• Los Alamos National Laboratory – Rod Borup, Plamen Atanassov (UNM)
• Oak Ridge National Laboratory – Karren More

Project Lead:
• Argonne National Laboratory - MSD – V.Stamenkovic / N.Markovic
Objectives The main focus of ongoing DOE Hydrogen & Fuel Cell Program is development of highly-efficient and durable Pt-Alloy catalysts for the ORR with low-Pt content

Relevance

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2011 Status</th>
<th>2020 Targets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum group metal total content (both electrodes)</td>
<td>g / kW (rated)</td>
<td>0.19</td>
<td>0.125</td>
</tr>
<tr>
<td>Platinum group metal (pgm) total loading</td>
<td>mg PGM / cm² electrode area</td>
<td>0.15</td>
<td>0.125</td>
</tr>
<tr>
<td>Loss in Initial catalytic activity</td>
<td>% mass activity loss</td>
<td>48</td>
<td>&lt;40</td>
</tr>
<tr>
<td>Electro catalyst support stability</td>
<td>% mass activity loss</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Mass activity</td>
<td>A / mg Pt @ 900 mV_{iR-free}</td>
<td>0.24</td>
<td>0.44</td>
</tr>
<tr>
<td>Non-Pt catalyst activity per volume of supported catalyst</td>
<td>A / cm³ @ 800 mV_{iR-free}</td>
<td>60 (measured at 0.8 V)</td>
<td>185 (extrapolated from &gt;0.85 V)</td>
</tr>
</tbody>
</table>

Source: Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan

ANL Technical Targets

- Total PGM loading
  2020 DOE target 0.125 mg_{PGM/cm²}
- Loss in initial mass activity
  2020 DOE target <40%
- Mass activity @ 0.9V_{iR-free}
  2020 DOE target 0.44 A/mg_{Pt}
Materials-by-design approach - to design, characterize, understand, synthesize/fabricate, test and develop tailored high performance low platinum-alloy nanoscale catalysts

Approach

- Rational synthesis based on well-defined systems
- Activity boost by lower surface coverage of spectators
- Addition of the elements that hinder Pt dissolution
- Prevent loss of TM atoms without activity decrease

**ANL**

PEMFC Cathode Catalysts Development
well-defined systems, fundamental principles, chemical and thin film synthesis, structural and RDE & MEA characterizations

Task
1° well-defined bulk and thin film surfaces of PtMN:
- single crystalline and polycrystalline systems
- structure/composition vs. activity/durability (UHV, PVD, STM vs. RDE, STM, ICP/MS)

2° synthesis of nano-, meso- and thinfilm- PtMN catalysts:
- shape/size/composition control
- intermetallics; core/interlayer/shell; thin-film systems (colloidal chemical synthesis, PVD, HRTEM/STEM)

3° electrochemical characterization of catalysts:
- optimization: ionomer/carbon/propanol/catalyst ink
- temperature effect; Ionic Liquid evaluation
- activity/durability in RDE vs. 5-50cm²/MEA; HRTEM

4° fine tuning of performance through catalyst-support:
- Carbon based materials

5° scaling-up of the most promising catalysts:
- gram scale single batches

**Inter Lab Collaborators**

**ANL/LBNL $200K**
Support of Scaling-Up

**LANL $150K**
Advanced supports

**LBWL $100K**
Catalyst Synthesis

**ORNL $50K**
Electron Microscopy

**LANL $50cm² MEA testing**

**LANL**

Support of Scaling-Up

**ANL/LBNL $200K**
Project Lead

**Task 1**
LEIS, AR-XPS, AES, UPS, LEED, STM

**Task 2&5**
Magnetron Sputtering

**Task 3**
Electrochemical Cell

**Task 4**
Electrochemical ICP/MS

**Task 5**
MEA test stand

scale-up synthesis of nanomaterials

grams of catalyst

solvo-thermal

advanced supports

**ANL**

Catalyst Synthesis

**LBNL**

$100K Catalyst Synthesis

**LANL**

$150K 50cm² MEA testing

**LANL**

Advanced supports

**ANL/LBNL $200K**
Support of Scaling-Up

**ORNL**

$50K Electron Microscopy
Approach

Project Management

<table>
<thead>
<tr>
<th>Table 1</th>
<th>FY16</th>
<th>FY17</th>
<th>FY18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active Task</td>
<td>Q1 Jan</td>
<td>Q2 Apr</td>
<td>Q3 July</td>
</tr>
<tr>
<td>T1 WDS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T2 SYN</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T3 ECC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T4 SUP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T5 SCA</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Task 1 - Well-Defined Systems (WDS)
Task 2 - Synthesis of Materials (SYN)
Task 3 - Electrochemical Characterization (ECC)
Task 4 - Novel Support/Catalyst (SUP)
Task 5 - Scaling Up of Materials (SCA)

- From fundamentals to real-world materials
- Simultaneous effort in five Tasks
- Go-No Go evaluation
- Progress measures are quarterly evaluated
Task 1  **Accomplishments and Progress:** 

**RDE-ICP/MS of Pt/C Nanoparticles**

**Surface Structure**

<table>
<thead>
<tr>
<th></th>
<th>Pt(111)</th>
<th>Pt(100)</th>
<th>Pt(110)</th>
<th>Pt-poly</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved Pt per cycle [$\mu$ML]</td>
<td>2</td>
<td>7</td>
<td>83</td>
<td>36</td>
</tr>
</tbody>
</table>

Detection Limit: $0.8 \mu$ML of Pt

**In-Situ RDE-ICP/MS**

Correlation between Surface Structure - Activity – Dissolution

Monodisperse 20% Pt/C NPs 3 and 5nm

P. P. Lopes, D. Strmcnik, J. Connell, V. R. Stamenkovic and N.M. Markovic

*ACS Catalysis, 6 (4), 2536-2544, 2016*
Electrode morphology ("2D" vs. 3D)

- Similar cluster/particle size
- Normalization by $H_{\text{upd}}$ : specific dissolution rate

Potential range: 0.05 to 1.0 V

$T = 25^\circ C$

3D morphology of Pt/C layer over GC enables redeposition of Pt and attenuates dissolution

Redeposition of Pt leads to the coarsening of particles as opposed to dissolution
Task 1: Accomplishments and Progress: EC-ICP-MS Pt-Surfaces effect of substrate

GC vs. Au vs. Pd

- Adding Pt on top of Pd decreases significantly Pd dissolution
- Subsurface of Pd improves Pt stability as compared to GC as substrate
- Improved stability for both metals
- Pd subsurface still dissolves through pinholes

Potential range: 0.05 to 1.0 V

T = 25°C
Task 1 Accomplishments and Progress:  
**In-Situ EC-ICP-MS**  
**Pt$_x$Ni$_{1-x}$ Alloys**

- **Presence of Pt promotes Ni stability**
- **Increasing Ni content enhances ORR activity**
- **Stability of Pt decreases with Ni content**
- **Optimal Ni conc. is 1:1**
Task 2-3 Accomplishments and Progress: \textit{PtNi Nanopinwheels / C}

\textit{in collaboration with K.L. More, ORNL}

\begin{itemize}
\item many channels and cavities
\item pinwheel 'petals' are hollow and/or folded over
\end{itemize}

\begin{itemize}
\item HAADF
\item Pt
\item Ni
\item overlay
\end{itemize}

\begin{itemize}
\item Specific Activity (mA/cm$^2$)
\item Mass Activity (A/mg)
\end{itemize}

\begin{itemize}
\item @0.95 V
\item @0.90 V
\item @0.95 V
\end{itemize}

\begin{itemize}
\item Current density (mA/cm$^2$)
\item Potential (V vs. RHE)
\end{itemize}

\begin{itemize}
\item @0.90 V
\item @0.90 V
\item @0.95 V
\item @0.95 V
\end{itemize}

\begin{itemize}
\item Argonne National Laboratory
\item Oak Ridge National Laboratory
\end{itemize}
Task 2  

Accomplishments and Progress:

PtNi Nanocage Structure

in collaboration with K.L. More, ORNL

PtNi solid polyhedra are converted into hollow nanocages after evolution treatment.
Task 2-3 Accomplishments and Progress: PtNi Nanocage Properties

Collab. with K.L. More, ORNL

The PtNi Nanocages show high ORR activity in RDE experiments

Evolution treatment

Specific Activity (mA/cm²) | Mass Activity (A/mgPt)
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.95 V</td>
<td>0.90 V</td>
</tr>
<tr>
<td>PtNi Nanocages</td>
<td>0.73</td>
</tr>
<tr>
<td>Pure Pt Nanocages (1)</td>
<td>1.98</td>
</tr>
</tbody>
</table>

The PtNi Nanocages show high ORR activity in RDE experiments
Task 2  
Accomplishments and Progress:  
*PtNi Nanoframes with Radial Joists*

in collaboration with K.L. More, ORNL

Different than the NFs
A new PtNi NFs with the radial joists

HAADF
Task 2: Accomplishments and Progress: 

**PtNi nanoframes with radial joists**

*in collaboration with K.L. More, ORNL*

**Structure analysis**

- Blender models: RD frame
- Radial joists to each vertex
- ...& deformation added:

*slices through volume center at different orientations:*

- Blender RD frame & joists
- Electron tomography

*Structure is slightly deformed (concave/excavated facets with wire frame) and contains additional linkages in the interior... connecting surface vertices to central point

*the similarity between the 3D cross-sections and cross sections of the modeled frame with radial joists suggests the majority of vertices are joined with the core, no major preference toward 100 (6x) or 111 vertices (8x)*

*slices through volume center of blender RD frame model with joists from each vertex to center (for reference):*
Task 2-3  
Accomplishments and Progress:  

PtNi Excavated Nanoframes  
in collaboration with Peidong Yang, LBNL

Scale bar = 20 nm
Scale bar = 5 nm

Hollow solid
Excavated solid
Hollow frame
Excavated frame
Scale bars = 10 nm

Specific Activity

\[
\begin{align*}
I_k (\text{mA/cm}^2) & : \\
Pt/C & : 0.0 \\
H-NF & : 0.5 \\
E-NF & : 1.5
\end{align*}
\]

Mass Activity

\[
\begin{align*}
I_m (\text{A/mgPt}) & : \\
Pt/C & : 0.0 \\
H-NF & : 0.5 \\
E-NF & : 0.8
\end{align*}
\]
**Task 5  Accomplishments and Progress:**

**Process R&D and Scale Up**
collab. with Greg Krumdick, ANL - MERF

### Timeline & Milestones

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>M 1-2</td>
<td>1) <strong>Hot-injection</strong> was avoid using one-pot synthesis. 2) Benzyl ether as solvent. <strong>No Go</strong></td>
</tr>
<tr>
<td>M 3</td>
<td>3) Phenyl ether as solvent. 4) Best synthesis condition was established. 5) Reproducibility was confirmed. <strong>Go</strong></td>
</tr>
<tr>
<td>M 4</td>
<td>6) 1st stage scale up (<strong>1 g / batch</strong>) was successful. 7) <strong>New method</strong> to load PtNi nanoparticles on carbon and its separation from solvent was developed.</td>
</tr>
<tr>
<td>M 5-6</td>
<td>8) Reproducibility of 1st stage scale up was confirmed. 9) Pre-annealing process was investigated.</td>
</tr>
<tr>
<td>M 6-7</td>
<td>10) Acid leaching process was modified. <strong>Go</strong></td>
</tr>
<tr>
<td>M 8-9</td>
<td>11) The 2nd stage scale up (<strong>5 g / batch</strong>) was successful. 12) Acid leaching process was further investigated.</td>
</tr>
<tr>
<td>M 10</td>
<td>13) The 2nd stage scale up is <strong>reproducible</strong>. <strong>Go</strong></td>
</tr>
<tr>
<td>M 11-12</td>
<td>14) MEA performance; New <strong>IP application</strong>; Sample send out; Manuscript preparation.</td>
</tr>
</tbody>
</table>
**Target: mono-disperse 5 nm PtNi**

**PtNi synthesis:**  
**0.1 g Scale**
1. Pre-heat mixture to 200 °C.  
Nickel acetate tetrahydrate (0.1667 g)  
1,2-Tetradecanediol (0.085 g)  
Oleic acid (0.4 ml) & Oleylamine (0.4 ml)  
Diphenyl ether (20 ml) or Dibenzyl ether (20 ml)  
2. Inject preheated Pt solution (~80 °C).  
Platinum(II) acetylacetonate (0.13 g)  
In 1,2-Dichlorobenzene (1.5 ml)  
3. Hold T at 200 °C for 1 h.  

**Loading on carbon:**  
**0.1 g Scale**
1. Mix and sonicate in Hexane or Chloroform.  
2. Evaporation of solvent.  
3. Precipitate PtNi/C with Hexane.  
4. Filtration.  

**Acid leaching:**  
**0.1 g Scale**
1. Sonicate and soak PtNi/C in 0.1 M HClO₄.  
2. Centrifuge.  

**One-pot**  
**5 g Scale**

200 °C  
30 min  
Nickel acetate tetrahydrate (2.5 g)  
1,2-Tetradecanediol (1.28 g)  
Oleic acid (7.5 ml) & Oleylamine (7.5 ml)  
Diphenyl ether (300 ml)  
Platinum(II) acetylacetonate (1.95 g)  
1,2-Dichlorobenzene (45 ml)  

**5 g scale**

**Process overview: 0.1 g vs. 5 g**

- Safer  
- Easier  
- Scalable  
- Reproducible
Task 5  Accomplishments and Progress:  One pot vs. Injection Diphenyl ether

in collaboration with Greg Krumdick, ANL -MERF

Better result from one-pot procedure
Particle sizes keep constant after 10 min reaction  Good for scale up
Desirable mono-dispersed 5 nm PtNi nanoparticles are obtained reproducibly.
Uniform distribution of PtNi nanoparticles on carbon was achieved using newly developed loading method.

More Ni left in PtNi nanoparticles with modified leaching process.
### Task 5: Accomplishments and Progress

**5 g Reproducibility-RDE/ECSA**

in collaboration with Greg Krumdick, ANL-MERF

<table>
<thead>
<tr>
<th></th>
<th>ECSA$_{HUPD}$ (cm$^2$)</th>
<th>ECSA$_{CO}$ (cm$^2$)</th>
<th>ECSA$<em>{CO}$/ECSA$</em>{HUPD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 g</td>
<td>0.684</td>
<td>0.946</td>
<td><strong>1.38</strong></td>
</tr>
<tr>
<td>5 g</td>
<td>0.672</td>
<td>0.923</td>
<td><strong>1.37</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Pt loading (%)</th>
<th>SSA$_{CO}$ (m$^2$/g)</th>
<th>Pt:Ni (atomic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 g</td>
<td>12.66</td>
<td>60</td>
<td><strong>1.37:1</strong></td>
</tr>
<tr>
<td>5 g</td>
<td>14.53</td>
<td>63.5</td>
<td><strong>1.35:1</strong></td>
</tr>
</tbody>
</table>

![Graphs showing CO stripping data for 4 g and 5 g samples.](image-url)
In-Situ EC-ICP-MS
Pt-Alloy NPs

Task 2,3,5

Accomplishments and Progress:

- Electrochemical stability of PtNi particles
- Similar Ni dissolution profiles for both nanoframes and scale-up particles
- No dissolution increase due to presence of O₂
- Pt dissolution on detection limit – favoring multilayered Pt surfaces

Potential range: 0.05 to 1.0 V

T = 25°C
Task 2-3  Accomplishments and Progress:

**scaled PtNi in 5cm² MEA**

*in collaboration with Debbie Myers, ANL/CSE and Karren More, ORNL*

Cathode Loading:

- 0.04 mg-Pt/cm²
- I/C = 0.8,
- H₂/O₂ (or Air),
- 80°C, 150 kPa(abs)
- 100%RH

<table>
<thead>
<tr>
<th>TKK 20 wt%Pt/C</th>
<th>Units</th>
<th>PtNi</th>
<th>TKK Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt total loading</td>
<td>mgPt/cm²</td>
<td>~0.04</td>
<td>~0.04</td>
</tr>
<tr>
<td>Mass activity (H₂-O₂)</td>
<td>A/mgPGM</td>
<td>0.5</td>
<td>0.22</td>
</tr>
<tr>
<td>Specific activity (H₂-O₂)</td>
<td>mA/cm²</td>
<td>1.01</td>
<td>0.39</td>
</tr>
<tr>
<td>MEA performance (H₂-Air)</td>
<td>mA/cm²</td>
<td>131.34</td>
<td>64.3</td>
</tr>
<tr>
<td>ECSA</td>
<td>m²/gPGM</td>
<td>50</td>
<td>52.5</td>
</tr>
</tbody>
</table>

Fresh:
- Pt at.% = 72%
- Ni at.% = 28%

Tested:
- Pt at.% = 80%
- Ni at.% = 20%
**PtNi/HSC 5cm² MEA Kinetics**

**ORR Mass Activity**
150 kPa, (100 kPa $p_O_2$), 100%RH, 80°C

---

**Electrochemical Analysis**

<table>
<thead>
<tr>
<th>Pt Loading (mg/cm² Pt)</th>
<th>0.05</th>
<th>0.11</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_m$ (mA/mgPt)</td>
<td>390</td>
<td>290</td>
</tr>
<tr>
<td>$I_s$ ($\mu$A/cm² Pt)</td>
<td>640</td>
<td>610</td>
</tr>
<tr>
<td>ECA (m²/gPt)</td>
<td>60</td>
<td>48</td>
</tr>
<tr>
<td>ECA CO (m²/gPt)</td>
<td>53</td>
<td>43</td>
</tr>
<tr>
<td>HFR ($m\Omega$-cm²)</td>
<td>45</td>
<td>43</td>
</tr>
</tbody>
</table>

---

**Task 3 Accomplishments and Progress:**

- Scaled PtNi in 5cm² MEA

  in collaboration with Shyam Kocha and Kenneth Neyerlin, NREL

---

**0.11 mg Pt/cm² CO Stripping**

80°C, 100% RH

---

**Graph**

- $E_{HFR}$-free
  - 0.11 mg Pt/cm² PtNi/HSC ANL
  - 0.05 mg Pt/cm² PtNi/HSC ANL

---

**Argonne National Laboratory**
Synthesis technique results in the majority of Pt sites available at lower RH — May have positive implications on RO$_2$Pt

Further studies in progress
Collaborations

**Lead:** design, synthesis, evaluation
**Sub:** synthesis, scale-up support
**Sub:** structural characterization
**Sub:** catalyst supports

**Lead:** process R&D and scale-up
**Sub:** process support

**Lead:** 5 and 25cm² MEA
**Sub:** 25 and 50cm² MEA

**OEMs**

**T2M**
Remaining Challenges and Barriers

- Differences between RDE and MEA, surface chemistry, ionomer catalyst interactions
- Temperature effect on performance activity/durability
- High current density region needs improvements for MEA
- Support – catalyst interactions
- Scale-up process for the most advanced structures

1) Durability of fuel cell stack (<40% activity loss)

2) Cost (total loading of PGM 0.125 mg$_{\text{PGM}}$ / cm$^2$)

3) Performance (mass activity @ 0.9V 0.44 A/mg$_{\text{Pt}}$)
Proposed Future Work

- **Alternative** approaches towards highly active and stable catalysts with low PGM content
- **Tailoring** of the structure/composition that can optimize durability/performance in Pt-alloys
- **Synthesis** of tailored low-PGM practical catalysts with alternative supports
- **Structural characterization** (in-situ XAS, HRTEM, XRD)
- **Resolving** the surface chemistry in MEA
- **Electrochemical** evaluation of performance (RDE, MEA)
- **In-situ** durability studies for novel catalyst-support structures (RDE-ICP/MS)
- **Scale-up** of chemical processes to produce gram quantities of the most promising catalysts
Technology Transfer Activities

- **United States Patent**
  - Patent No.: US 8,781,738 B2
  - Date of Patent: Jan. 18, 2011

- **Auto OEMs**
  - Process scale-up

- **Catalysts Scale Up**
  - 3 NDA signed
  - FY17

- **Constant build up of IP portfolio**
  - 5 issued patents, 3 pending
SUMMARY

Approach

- From fundamentals to real-world materials
- Focus on addressing DOE Technical Targets
- Link between electrocatalysis in the RDE vs. MEA
- Rational design and synthesis of advanced materials with low content of precious metals

Accomplishments

- Established routine operations in a new Scale-Up process Lab and new RDE-ICP/MS
- Dissolution of Pt from 2D thin film surfaces vs. 3D Pt/C catalyst layers
- Addition of both subsurface Au or Pd diminishes Pt dissolution
- Established stability trend for Pt_xNi_1-x and particle size dependence for Pt/C
- Novel nanoscale structures with superior electrochemical properties have been synthesized
- In-situ RDE-ICP/MS revealed stability of highly active PtNi catalysts with multilayered Pt-Skin surfaces
- Scaled reproducible synthesis process of 5 grams per batch for PtNi/C with multilayered Pt-Skin surfaces
- Scaled catalyst is monodisperse with advanced catalytic properties in both RDE and MEA
- PtNi with multilayered Pt-Skin exceeded DOE 2020 Technical Target for mass activity and durability in MEA
- One patent application in FY17, 2 articles published and 6 presentations at conferences

Collaborations

- Collaborative effort among the teams from four national laboratories is executed simultaneously in five tasks
- Ongoing exchange with Auto-OEMs and stake holders
- Numerous contacts and collaborative exchanges with academia and other national laboratories
Publications and Presentations FY17

2 Publications
6 Presentations
2 patent applications

Full time postdocs: Dr. Dongguo Li (RDE, synthesis, thin films)
Dr. Haifeng Lv (RDE, synthesis, MEA)
Dr. Rongyue Wang (scale up synthesis, RDE, MEA)

Partial time postdocs: Dr. Pietro Papa Lopes (RDE-ICP-MS)

Partial time Staff: Paul Paulikas (UHV, thin films), Krzysztof Pupek

Grad student: Nigel Becknell (synthesis, RDE, EXAFS)