Tailored High Performance Low-PGM Alloy Cathode Catalysts

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     Nenad M. Markovic

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 FY16: $1.2M

**Overview**

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**Barriers to be addressed**

1. **Durability** of fuel cell stack (<40% activity loss)
2. **Cost** (total loading of PGM 0.125 mg_{PGM} / cm^2)
3. **Performance** (mass activity @ 0.9V 0.44 A/mg_{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*

### Table 3.4.13 Technical Targets: Electrocatalysts for Transportation Applications

<table>
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<tr>
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<th>Units</th>
<th>2011 Status</th>
<th>2020 Targets</th>
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<tbody>
<tr>
<td>Platinum group metal total content (both electrodes)</td>
<td>g / kW (rated)</td>
<td>0.19(^b)</td>
<td>0.125</td>
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<td>Platinum group metal (pgm) total loading</td>
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<td>Loss in Initial catalytic activity</td>
<td>% mass activity loss</td>
<td>48(^b)</td>
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<td>Electro catalyst support stability</td>
<td>% mass activity loss</td>
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<td>A / mg Pt @ 900 mV(_{IR-free})</td>
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<td>A / cm(^3) @ 800 mV(_{IR-free})</td>
<td>60 (measured at 0.8 V)(^b)</td>
<td>165 (extrapolated from &gt;0.85 V)(^b)</td>
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*Source: Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan*
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### ANL Technical Targets

- **Total PGM loading**
  
  2020 DOE target 0.125 mg_{PGM/cm^2}

- **Loss in initial mass activity**
  
  2020 DOE target <40%

- **Mass activity @ 0.9V_{iR-free}**
  
  2020 DOE target 0.44 A/mg_{Pt}

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- Non-Pt catalyst activity per volume of supported catalyst
  
  A / cm\(^3\) @ 800 mV_{iR-free} 300 (measured at 0.8 V) 185 (extrapolated from >0.85 V) 300

**Source:** Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan
**Materials-by-design approach** - to design, characterize, understand, synthesize/fabricate, test and develop tailored high performance low platinum-alloy nanoscale catalysts

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**Approach**

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

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**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)

**Task 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)

**Task 3**

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

**Task 4**

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

**Task 5**

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

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**Support of Scaling-Up**

**ANL/LBNL** $200K

**LANL** $150K

**50 cm² MEA testing**

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**Project Lead**

**Inter Lab Collaborators**

**LBNL** $100K

**Catalyst Synthesis**

**ORNL** $50K

**Electron Microscopy**

**LANL** $150K

**Advanced supports**

**ANL/LBNL** $200K

**Support of Scaling-Up**

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**Electrochemical Cell**

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

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**Electrochemical ICP/MS**

**Quadrupole mass filter**

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**Magnetron Sputtering**

**Nano-, meso- and thinfilm PtMN catalysts:**

- shape/size/composition control
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Approach

- Single Crystals
- Solid Nanoparticles
- NPs with Skin Surfaces
- Core-Shell Nanoparticles
- Meso-S Thin Films
- Nanoframes and Nanowires
- Shaped Particles
- Core-Shell Nanoparticles

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></td>
<td></td>
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<tr>
<td>T1</td>
<td>WDS</td>
<td>Jan</td>
<td></td>
</tr>
<tr>
<td>T2</td>
<td>SYN</td>
<td></td>
<td>Apr</td>
</tr>
<tr>
<td>T3</td>
<td>ECC</td>
<td></td>
<td>July</td>
</tr>
<tr>
<td>T4</td>
<td>SUP</td>
<td></td>
<td>Oct</td>
</tr>
<tr>
<td>T5</td>
<td>SCA</td>
<td></td>
<td></td>
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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
- Go-No Go evaluation
- Simultaneous effort in five Tasks
- Progress measures are quarterly evaluated
Total Pt loss over one potential cycle up to 1.05 V for distinct Pt surface morphologies, indicating the stability trend follows the coordination number of the surface sites.

<table>
<thead>
<tr>
<th>Pt Surface</th>
<th>Dissolved Pt per cycle [μML]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(111)</td>
<td>2</td>
</tr>
<tr>
<td>Pt(100)</td>
<td>7</td>
</tr>
<tr>
<td>Pt(110)</td>
<td>83</td>
</tr>
<tr>
<td>Pt-poly</td>
<td>36</td>
</tr>
<tr>
<td>Pt/C</td>
<td>103*</td>
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</table>
1º Accomplishments and Progress: *In-Situ EC-ICP-MS* Pt-Surface/Au Subsurface

**GC-Pt(4ML)**

- Subsurface Au diminishes dissolution of Pt in each cycle

**GC-Au-Pt(4ML)**

- Dissolution of Pt in each cycle

Subsurface Au diminishes dissolution of Pt.
2° Accomplishments and Progress: **Catalysts Structures with Subsurface Au**

- **2011**: Au core- PtNi shell
- **2014**: Ni/Au IL/ PtNi shell

Subsurface Au does not alter catalytic properties of NPs

**Pt-Skeleton Surface**

Existence of Au surface atoms lowers the number of Pt active sites for adsorption of O$_2$

**After 400 °C annealing**

- **Au-PtNi**
- **Au$_X$-PtNi**

Addition of element in the core prevents segregation of Au over Pt after annealing

Annealing induces formation of Pt-Skin structure

Au remains in the subsurface
2º Accomplishments and Progress: **Catalysts Structures with Subsurface Au**

Au-X / NiPt-Skin Thin Film Structures

- Fine tuning of activity & durability
- Thickness of the PtNi shell
- Thickness/composition of Au-X subsurface
- Annealing temperature

Sample 4 of AuX/NiPt-Skin after 10K cycles to OCP shows the best activity-stability at room temperature

Input to nanoscale synthesis about the structure/composition of the core-shell catalyst
Accomplishments and Progress: \( \text{Pt}_3\text{Co catalysts Structures} \)

in collaboration with M. Chi and K.L. More, ORNL

HAADF and EDS elemental mapping

Dynamic of structural and chemical evolution at the atomic scale of \( \text{Pt}_3\text{Co NPs} \) during in-situ annealing distinct behavior at critical stages:

- \{111\}, \{110\}, \{100\} facets play different roles during the evolution of structure
- formation of a Pt-Skin shell with an alloyed disordered core;
- the nucleation of ordered domains;
- the establishment of an ordered L1\(_2\) phase followed by pre-melting

Nature Communications 6 (2015) No. 8925
PtCo Structures Towards Intermetallics

Accomplishments and Progress:

PtCo (L1₀) has even better performance than the intermetallic Pt₃Co (L₁₂) \(^*\)

Nat. Mat. 12, 81–87 (2013)

It is expected that PtCo (L₁₀) has even better performance than the intermetallic Pt₃Co (L₁₂) \(^*\)

Nat. Mat. 12, 81–87 (2013)
3º Accomplishments and Progress: PtCo Structures Towards Intermetallics

It is expected that PtCo (L10) has even better performance than the intermetallic Pt₃Co (L1₂)* Nat. Mat. 12, 81–87 (2013)
3º Accomplishments and Progress: **PtCo Towards Novel Structures**

in collaboration with Peidong Yang, LBNL

**Pt seed**

Pt@\(m\)-SiO\(_2\)

Add Co

Anneal

Ordered Pt\(_3\)Co@\(m\)-SiO\(_2\)

**3-D Intermetallic Nanostructures for Enhanced ORR Stability**

- **Pt seed**
- **Pt@\(m\)-SiO\(_2\)**
- **Ordered Pt\(_3\)Co@\(m\)-SiO\(_2\)**

**TEOS**

**HAADF**

**XRD:** Converted to intermetallic Pt\(_3\)Co after annealing treatment

- **SiO\(_2\)** coating allows high T annealing w/o agglomeration
- High surface to volume ratio
- 1-D branches protruding from the core
- Elongated highly crystalline surfaces with Pt-Skin topmost layer
- Tunable composition and structure, including intermetallics
Accomplishments and Progress:

PtNi Nanoframe Surface Structure

in collaboration with Peidong Yang, LBNL

PtNi(1.0) has a larger extent of alloying vs. Pt3Ni(1.5), including surface Ni that becomes NiO
Pt3Ni(1.5) has significant segregation of Pt with smoother morphology and the thickness of at least two atomic layers
Pt3Ni(1.0) has a thinner, rougher Pt surface caused by insufficient segregation of Pt to the surface
Pt3Ni(1.5) exhibits extremely high ORR activity due to its significant segregation of Pt, forming of a Pt-skin

In situ EXAFS:

Pt3Ni(1.0) = \( Q_{CO} / Q_{Hupd} = 1.0 \)
Pt3Ni(1.5) = \( Q_{CO} / Q_{Hupd} = 1.5 \)
ORR rate: Pt3Ni(1.0) < Pt3Ni(1.5)

N. Becknell, Y. Kang, Chen Chen, J. Resasco, N. Kornienko, J. Guo, N.M. Markovic, G.A. Somorjai, V.R. Stamenkovic, P. Yang
JACS 137 (2015) 15817
4º Accomplishments and Progress: **Multimetallic Nanoframes**

*in collaboration with Peidong Yang, LBNL*

**Ternary Metal Nanoframes**

Solid Pt-Ni dodecahedra

Metal precursors

Composition tuning to Pt-Ni-Fe, Pt-Ni-Rh, Pt-Ni-Mo etc.

1% Fe

3% Fe

5% Fe
5° Accomplishments and Progress:  

Process R&D and Scale Up

in collaboration with Greg Krumdick, ANL -MERF

- Argonne's Material Engineering Research Facility (MERF) was tasked with scaling up the new materials.
- The current process used in the discovery laboratory will be reviewed and scrutinized for scale up utility.
- MERF will conduct process R&D and develop scalable process for producing the material.
- The materials will be validated on each stage of scale up process and performance compared with the original sample.
- Detailed procedures for synthetizing, characterizing, and evaluating will be compiled into Technology Transfer Package.
- The materials will be available for both basic researches and industrial evaluators.
5° Accomplishments and Progress:  

Process R&D and Scale Up

in collaboration with Greg Krumdick, ANL-MERF

- Initial process R&D will focus on batch NP synthesis.
  - Investigate temperature and rate of addition on NP characteristic.
  - Nucleation rate vs. addition rate.
  - Improve safety of the process.
- Material selected for scale up is multilayered Pt-skin NP (Lab scale—0.1 g catalyst).
- 1st stage of scale up—1 g catalyst.
- 2nd stage of scale up—5 g catalyst.

Future target is to develop continuous process (flow reactor).
- Fast mass and heat transfer.
- Accurate control of reaction temperature and duration.
- Allow rapid optimization of reaction parameters.
- Low usage of reagents in the optimization process.
- Easy scalability by duplicating.
- Capability for online quality monitoring.
6° Accomplishments and Progress: \textit{PtNi with Multilayered Pt-Skin}

1. Raise T to 200 °C
   - Nickel acetate
   - 1,2-Tetradecanediol
   - Oleic acid
   - Oleylamine
   - Diphenyl ether

2. Add Pt source

Leaching
Leached PtNi nanoparticles
Annealing
Multilayered Pt-skin NP

Multiple Batches
200mg each
1 g of catalyst / 2 days
quality/performance matches small scale synthesis

RDE: PtNi with multilayered Skin in >7 more active than Pt/C

<table>
<thead>
<tr>
<th>Performance</th>
<th>PtNi</th>
<th>TKK Pt</th>
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<tr>
<td>Specific Activity</td>
<td>5.30/0.68</td>
<td>0.78/0.11</td>
</tr>
<tr>
<td>0.9V/0.95V (mA/cm²)</td>
<td></td>
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<td>Mass Activity</td>
<td>3.5/0.49</td>
<td>0.56/0.11</td>
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<td>0.9V/0.95V (A/mg)</td>
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6° Accomplishments and Progress: PtNi MEA Characterization

in collaboration with Debbie Myers, ANL - CSE

Cathode Loading: 0.046 mg-Pt/cm²
I/C = 1, H₂/O₂ (or Air), 80°C, 150 kPa(abs), 100%RH

TKK 20 wt%Pt/C
PtNi 16.7 wt%Pt/C

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<th>TKK Pt</th>
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<td>Pt loading</td>
<td>mg_PGM/cm²_geo</td>
<td>0.045</td>
<td>0.045</td>
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<tr>
<td>Mass Activity (H₂-O₂)</td>
<td>A/mg_PGM @ 0.9 V_{IR-free}</td>
<td>0.60</td>
<td>0.27</td>
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<tr>
<td>Specific Activity (H₂-O₂)</td>
<td>mA/cm²_PGM @ 0.9 V_{IR-free}</td>
<td>1.85</td>
<td>0.39</td>
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<tr>
<td>MEA performance (H₂-Air)</td>
<td>mA/cm² @ 0.8 V</td>
<td>101</td>
<td>47</td>
</tr>
<tr>
<td>ECSA</td>
<td>m²/g_PGM</td>
<td>35.10</td>
<td>52.5</td>
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<td>Collaborations</td>
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**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

**Sub:** catalyst supports

---

**Lead:** 5 and 25cm² MEA

**Sub:** 25 and 50cm² MEA

**OEMs**

**T2M**

**Catalysts Scale Up**

---

**MEA**

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

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

3) **Performance** (mass activity @ 0.9V 0.44 A/mg\(_{\text{Pt}}\))

- **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
Proposed Future Work

- Evaluation of activity/durability and optimization of MEA protocols at ANL and LANL
- 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

- Constant build up of IP portfolio
  - 5 issued patents, 4 pending

Auto OEMs in FY16
- Four OEM visits
- 3 NDA signed
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 three new labs since 10/2015: EC-ICP/MS, MEA and Scale-Up process Lab
- Quantified durability, atom-by-atom on different Pt surfaces
- Surfaces with highly corrugated morphology are less stable (Pt-Skeleton)
- Addition of subsurface Au diminishes Pt dissolution
- Novel Au core structures allow annealing of Pt-alloy shell w/o segregation Au while Pt-skin is formed
- In-situ annealing of Pt-alloy NP reveal transition from disordered alloy, Pt overlayer (Pt-Skin) to intermetallics
- Novel intermetallic structures with promising electrochemical properties have been synthesized
- In-situ EXAFS revealed the real surface structure of highly active PtNi nanoframe catalysts
- PtNi with multilayered Pt-Skin exceeded DOE 2020 Technical Target for mass activity and durability in MEA
- One patent issued in 2016, 5 articles published and 4 presentations at conferences

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

**FY16**

5 Publications
4 Presentations
1 issued US patent
3 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)

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