Contiguous Platinum Monolayer Oxygen Reduction Electrocatalysts on High-Stability-Low-Cost Supports

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Brookhaven National Laboratory

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Overview

Timeline
Start: July 2009
End: Project continuation and direction determined annually by DOE
% completed N/A

Budget
Funding received in FY14:
$ 650,000
Planned Funding in FY 15:
$ 650,000

Barriers
Catalysts’ Performance:
Catalyst activity; ≥ 0.44 A/mg_{PGM}
Catalysts’ Cost:
PGM loading; ≤ 0.125 mg PGM /cm^2
Catalysts’ Durability:
< 40% loss in activity under potential cycling

Collaborations
Toyota M. C., General Motors, LLC,
U. Wisconsin, U. Stony Brook, CFN-BNL, IRD- Fuel Cells,
Korean Institute for Energy Research
Project objectives:

Synthesizing high performance Pt monolayer (ML) on stable, inexpensive metal or alloy nanostructured electrocatalysts for the oxygen reduction reaction (ORR)

This reporting period:

Increasing activity and stability of Pt monolayer catalysts to meet the DOE technical targets for 2020 by following:

- Electrodeposition of inexpensive refractory metal alloy nanoparticles on GDLs to fabricate the electrodes of 5, 25, and 50 cm² and carrying out MEA tests at BNL and GM.

- Further developing the nitriding method to stabilize cores (Pd-Ni) and the stabilization method involving addition of Au to cores.

- Demonstrating suitability of Graphene as support for Pt ML catalysts
**Approach**

**Milestone 1: Verifying new improved synthetic methods**
- Depositing nearly perfect Pt MLs on various cores: **100%**
- Ordering core-monolayer shell interface structure: **90%**
- Nitriding non-noble metal core components for increased stability: **80%**

**Milestone 2: Fabrication of MEAs and tests of selected catalysts**
- MEA test of Pt/Pd synthesized in ethanol has a PGM activity of 0.4 A/mg; Pt mass activity 0.9 A/mg$_{Pt}$, at 900mV in O$_2$: **90%**
- Pulse – potential deposition of cores on GDL carbon used to obtain 5, 25 and 50 cm$^2$ electrodes: **90%**

**Milestone 3: The 100% Pt utilization**
- The 100% Pt utilizations has been verified in electrodeposited cores and nanoparticle cores deposited at GDL: **100%**

**Milestone 4: Graphene as support**
- Graphene and reduced Graphene Oxide were successfully used as supports: **50%**
Accomplishments and Progress: New syntheses of improved catalysts

Co-deposition of W-Ni cores, of the Pt/Pd/WNi catalyst - (Part of Ni displaced by Pd, Pt monolayer placed by UPD Cu displacement)

Durability of 5 cm² MEA in H₂/O₂ and H₂/Air

Accomplishment and Progress:

New syntheses of improved catalysts

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## Accomplishments and Progress: New syntheses of improved catalysts

### Durability assessment - summary

<table>
<thead>
<tr>
<th></th>
<th>DOE 2020 targets</th>
<th>Pt\text{ML}/Pd/WNi/GDL 80\textdegree C, H\textsubscript{2}/O\textsubscript{2}, 150 kPa</th>
<th>Pt\text{ML}/Pd/WNi/GDL 80\textdegree C, H\textsubscript{2}/O\textsubscript{2}, 300 kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGM total loading, mg\textsubscript{PGM}/cm\textsuperscript{2}</td>
<td>&lt; 0.125</td>
<td>0.07 mg\textsubscript{PGM} /cm\textsuperscript{2} at the cathode</td>
<td>0.07 mg\textsubscript{PGM} /cm\textsuperscript{2} at the cathode</td>
</tr>
<tr>
<td>Loss in performance at 0.8 A/cm\textsuperscript{2}</td>
<td>&lt; 30 mV</td>
<td>19 mV after 34000 AST</td>
<td>7 mV after 34000 AST</td>
</tr>
<tr>
<td>Loss in performance at 1.5 A/cm\textsuperscript{2}</td>
<td>&lt; 30 mV</td>
<td>22 mV after 34000 AST</td>
<td>19 mV after 34000 AST</td>
</tr>
<tr>
<td>Mass activity @900 mV\textsubscript{iR free}, A/mg\textsubscript{PGM}</td>
<td>&gt;0.44</td>
<td>0.37</td>
<td>0.46</td>
</tr>
</tbody>
</table>

- Achieved lower PGM loading, and high Pt utilization
- Surpassed the DOE targets for mass activity, and loss in performance at higher back pressure
- The performance in Air needs to be further improved
Accomplishments and Progress: New syntheses of improved catalysts

Co-deposition of W-Ni cores, of the Pt/Pd/WNi catalyst

Performance assessment of 50 cm² MEA

Polarization curves of 50 cm² MEA, assembled with Pt₅ML/Pd/WNi/GDL cathode, standard Pt/C (TKK 46 %) anode, and Nafion® XL membrane.

- Mass activity @ 900mV, iR-free – 0.41 A/mg_{PGM}
- The performance in Air needs to be improved
Accomplishments and Progress: New syntheses of improved catalysts

Electrodeposition of **dendritic Pd cores** for zero back pressure of O₂

Polarization curves of 5 cm² MEA with Ptₘₐₜ/Pd/GDL (dendritic Pd nanostructures) cathode, standard Pt/C (TKK 46 %) anode, and Nafion® HP membrane

Electrodeposition of dendritic nanostructured cores is a promising strategy for improving the MEAs performance at low or no back pressure, high current density, in H₂/Air feed.

*Dendritic Pd deposit, 113 m²/grₚₜ*
Accomplishments and Progress: New syntheses of improved catalysts

Carbon-supported PtPd dendritic catalysts

- Synthesized by galvanic replacement of Pd on Pd octahedral template nanoparticles by Pt.
- Surfactant: CTAC (cetyltrimethylammonium chloride)
- Reductant: ascorbic acid

![Image of synthesized catalyst](image_url)

Hong et al., 6(3) ACS Nano, 2410

![Graph showing electrochemical data](graph_url)

- MA: 0.57 A/mg_{Pt}
- 0.39 A/mg_{PGM}
- SA: 7.9 A/m^2
Using Au to stabilize various cores
Pt$_{\text{ML}}$ on Au-modified W compounds

Thermal procedure to modify cores

- Pt ML on Au-W compounds shows enhanced ORR performance
- No degradation in 30,000 cycles - high stability - selected for further tests

Pt Mass Activity: 0.72 A/mg$_{\text{Pt}}$
(Pt + Au) Mass Activity: 0.33 A/mg

Accomplishments and Progress: New syntheses of improved catalysts
Accomplishments and Progress: **Nitride-stabilized non-noble** core components

**Pt\textsubscript{ML}** on nitride-stabilized PdNi core catalysts

- \(\text{Pd}_{50}\text{Ni}_{50}/\text{C}\) calcinated in \(\text{N}_2\) at 250° C for 1 hr and in \(\text{NH}_3\) at 510° C for 2 hrs
- STEM/EELS show that Pd atoms segregate on the surfaces
- XAS shows a decrease in Ni bonding due to the formation of Ni nitride
Accomplishments and Progress: **Nitride-stabilized** non-noble core components

**Pt\textsubscript{ML}** on nitride-stabilized PdNi core catalysts

**Stability**: Ni nitride formation stabilizes Ni

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**Catalyst**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt\textsubscript{ML} Pd\textsubscript{50}Ni\textsubscript{50}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt mass activity</td>
<td>1.05 jk/ A mg\textsuperscript{-1}</td>
</tr>
<tr>
<td>PGM mass activity</td>
<td>0.61 jk/ A mg\textsuperscript{-1}</td>
</tr>
<tr>
<td>Specific activity</td>
<td>1.17 mA/cm\textsuperscript{2}</td>
</tr>
<tr>
<td>ECSA</td>
<td>90 m\textsuperscript{2}/g \textsubscript{Pt}</td>
</tr>
<tr>
<td>Particle size</td>
<td>13 nm</td>
</tr>
<tr>
<td>(E_{1/2}/(mV)) Initial/ After 50,000 cycles</td>
<td>850 / 840</td>
</tr>
</tbody>
</table>

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Pd content is reduced by 50\% in comparison with Pt/Pd/C catalyst, while stability and activity are enhanced.

Accomplishments and Progress: Adsorption of fluorinated molecules at Pt and ORR

At small coverage of CF₃, a negligible enhancement is observed; inhibition at larger approach deserves a short additional attention.

Expected decrease of H₂O activity on Pt similarly as in Yeager’s “dry cave” proposition.


Accomplishments and Progress: Graphene as catalysts support

ORR on Pt on annealed Fe Porphyrine (FeP) on Graphene (Gr)

Motivation: Electronic properties of graphene are easily modified by dopants and affect Pt monolayer

Annealing of 5% of FeP on Gr at 700°C in NH₃

<table>
<thead>
<tr>
<th>E₁/₂ (mV)</th>
<th>A/mgPt</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeP</td>
<td>633</td>
</tr>
<tr>
<td>Pt/FeP</td>
<td>838</td>
</tr>
<tr>
<td>Pt/FeP 5000 cycles</td>
<td>853</td>
</tr>
<tr>
<td>Pt/FeP 25000 cycles</td>
<td>869</td>
</tr>
</tbody>
</table>

Potential pulse deposition of Pt

Pt loading: 2.1 µg/cm²

RDE loading 0.2 mg/cm²

Potential cycling at 50 mV/s from 0.6-1.0 V in air

FeP on Gr shows an excellent performance in alkaline solutions
Accomplishments and Progress: Graphene as catalysts support

Potential pulse Pt deposition on 5% FeP on Graphene

Nucleation of Pt occurs preferentially on Fe;

STEM-HAADF image and EDS of particles after 25,000 cycles show large Fe and small Pt particles.
Accomplishments and Progress: Graphene as catalysts support

Pt ML on Pd core on reduced Graphene oxide (rGO)

Pd deposited on Reduced Graphene oxide using Cation, Pb$^{2+}$, adsorption, Pb$^{0}$ displacement method.

0.1 M HClO$_4$

$E_{1/2} = 0.870$V

Clusters of Pb deposited on rGO are smaller than 1 nm.

Atomic level control of metal deposition using Cation adsorption/reduction, atom displacement is possible with rGO; MEA with rGO has promising properties

Half Wave potential: 870 mV
Pt Mass Activity: 0.8 A/mg

Cathode- Pt/Pd/GO with PGM loading of 0.114 mg/cm$^2$; $MA_{pgm} = 0.3$ A/mg - activation was not sufficient
Pt deposited on Au using Cu upd technique
Pt: 2.1 μg/cm²
Pt mass activity after 5000 cycles: 0.6 A/mg

Activity increases, no change in surface area
Technical Accomplishments and Progress

Facile synthesis of unsupported RuO$_2$ and Ru$_{0.5}$Ir$_{0.5}$O$_2$ for oxygen evolution

Formed with a spike of high temperature while carbon is burned out within 10 min, the metal oxide particles are small in size and highly ordered compared to other thermal synthesis methods, which are important for obtaining a high surface area, durable oxide nanocatalysts.

Ru$_{0.5}$Ir$_{0.5}$O$_2$ is more active than IrO$_2$ over large potential region.

**Average diameter:** 3.3 nm

**RuO$_2$**

**Ru/C**

**Ru/C + H$_2$IrCl$_6$**

400 $^\circ$C in air, 1 h

**Ru$_{0.5}$Ir$_{0.5}$O$_2$**

Some core-shell, some mixed

Clean, ordered, uniform RuO$_2$
Summary

Improvements of Pt ML catalysts, increased understanding of MEAs fabrication, developing new cores and stabilization methods, and using Graphene as support have been accomplished.

Pulse – potential deposition of cores on GDL carbon used to obtain 5, 25 and 50 cm$^2$ electrodes; the procedure has been further improved.

The MEA mass activity and durability of some catalysts exceed the DOE 2020 targets. Air performance needs improvement.

Stabilization of cores based on nitriding method and Au addition has been improved.

Dendritic deposits cores provide enhanced mass transport conditions for air and improve performance at high current densities.

At small coverage, short chain fluorinated molecules cause a negligible enhancement of the ORR; inhibition is observed at larger ones.

Graphene and reduced Graphene Oxide can be useful supports. Atomic level control of metal deposition using $Cation$ adsorption/reduction, $atom$ displacement is possible.

High activity Ru$_{0.5}$-Ir$_{0.5}$O$_2$ catalyst for the OER has been developed.
Proposed Future Work

FY 15 and beyond

1. Synthesis and MEA tests
   Selected Pt ML on nitride, or Au stabilized cores of non-noble and refractory metal alloy, and Graphene-supported cores in 50 cm² electrodes. Tests are at BNL and GM.
   
   **Milestone one** ------------------------------------------------------------- Completed 30%

2. Stack tests at GM
   Pt_{ML}/Pd/WNi and the catalysts selected from the above MEA tests.
   
   **Milestone two** ------------------------------------------------------------- Completed 20%

3. Novel strategies to synthesize high performance, Pt monolayer electrocatalysts
   Electrodeposition of refractory metal alloys using aqueous and/or **non-aqueous solvents**.
   Nitriding to stabilize non-noble metal cores. Nitriding at **high pressure**.
   Graphine as tunable nanoparticle support.
   Reactive spray deposition of non-noble metal alloys **without oxidation of components**.
   
   **Milestone three** ------------------------------------------------------------- Completed 30%

4. Approaching 1.23V
   Onion-structured nanoparticles with new cores of multiple metal layers to tune Pt monolayer properties and shift E° closer to 1.23 V. Supporting DFT calculations have been completed.
   
   **Milestone four** ------------------------------------------------------------- Completed 20%
Collaborations

Toyota Motor Company (Industry) Makoto Adachi, Toshihiko Yoshida MEA tests.

U. Wisconsin (University) Manos Mavrikakis, collaboration on theoretical calculations

U. Connecticut, Radenka Maric, reactive spray catalysts deposition

Center for Functional Nanomaterials, BNL Ping Liu, DFT calculations; Eli Sutter, Dong Su and Yimei Zhu, TEM, STEM

GM (Industry) Anu Kongkanand, Yun Cai

IRD Fuel Cells, (Industry) Madeleine Odgaard

Korean Institute for Energy Research, Gu-Gon Park

Technology Transfer
Publications


Patents


Responses to the Previous Year’s Reviewers’ Comments

Q1 Pure transition metal cores should be excluded from the scope; it has been shown multiple times that they dissolve.

A1 We agree with the view on dissolution of non-noble metal cores. For that reason we are developing ordered intermetallic compounds, gold alloys and nitride-stabilized core constituents. Stability of these species is being determined in current MEA tests.

Q2 It would be nice to see the high stability of the nitride-stabilized Pt-M core-shell catalyst in MEA. A benchmark against commercial Pt/C and PtCo/C with similar Pt loading is missing.

A2 These experiments are being conducted. The delay was caused by relocation of the laboratory.

Q3 Improvement in air performance would be good.

A3 Yes, we are redesigning the electrode structure to improve it. Guidelines provided by dendritic porous deposits. It works with air without back-pressure.

Q4 The hollow core-shell concept was expected to see progress.

A4 This topic won BNL’s technology maturation project and is being researched intensively. We will mention it in the presentation.
Technical back-up slides
PtML on Au deposited on rGO (after 20,000 potential cycles)
ORR on Fe Porphyrin on Graphene treated in Ammonia at 900°C

Pt loading: 6.0 ug/cm²
FeP + graphene loading: 0.4 mg/cm²

Half-wave potentials @1600 rpm
ETEK Pt/C : 840mV
Fe P/G : 868 mV
## ORR on Metal Porphyrins on Graphene in 0.1 M KOH

<table>
<thead>
<tr>
<th>Catalyst / (loading)</th>
<th>Onset Potential (V)</th>
<th>Half Wave Potential (mV)</th>
<th>Half Wave Potential after <strong>5000 cycles</strong> (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFeP/G (0.4 mg/cm²)</td>
<td>0.97</td>
<td>880</td>
<td>867</td>
</tr>
<tr>
<td>CoP/G (0.4 mg/cm²)</td>
<td>0.92</td>
<td>845</td>
<td>840</td>
</tr>
<tr>
<td>FeP/G (0.4 mg/cm²)</td>
<td>0.99</td>
<td>870</td>
<td>860</td>
</tr>
<tr>
<td>Pt/C (0.1 mg/cm²) Pt: 10.2 ug/cm²</td>
<td>0.97</td>
<td>868</td>
<td>838</td>
</tr>
</tbody>
</table>

Electrolyte: 0.1 M KOH; Scan rate: 10mV/s; Cycling: 0.65 – 1.0 V in air
Technical backup

Facile synthesis of unsupported RuO₂ and Ru₀.₅Ir₀.₅O₂

The Adams fusion method produces stable IrO₂ nanoparticles with high surface area, but often contains some Ir metal particles due to inhomogeneity in the mixture of H₂IrCl₆ (metal precursor) and NaNO₃ (oxidant).

We used carbon powder as the template to make completely oxidized Ru and Ru₀.₅Ir₀.₅O₂ nanocatalysts. Carbon was completely eliminated from Ru/C after Ru oxidization in air at 350-450°C as the weight changes were consistent with the value calculated using the mass for two oxygen per Ru minus the weight of carbon when we used Ru/C with Ru weight percent between 20-40%.

The Ru₀.₅Ir₀.₅O₂ catalyst was made by mixing Ru/C with H₂IrCl₆ in ethanol solution and dried at 80°C before calcinated at 400°C for 1h. The weight of obtained catalyst was also consistent with that for RuO₂ and IrO₂ without carbon.

<table>
<thead>
<tr>
<th>Ru/C mg</th>
<th>Ru wt%</th>
<th>Ru mmol</th>
<th>RuO₂ mg</th>
<th>Ir mmol</th>
<th>IrO₂ mg</th>
<th>sum mg</th>
<th>weight mg</th>
<th>deviation %</th>
<th>Temp °C</th>
<th>time min</th>
</tr>
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<tbody>
<tr>
<td>70.9</td>
<td>40</td>
<td>281</td>
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