Non-Platinum Bimetallic Cathode Electrocatalysts

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Argonne National Laboratory

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This presentation does not contain any proprietary or confidential information
Overview

Timeline
- Project start data: January, 2007
- Project end data: December, 2010
- Percentage complete: 80%

Budget
- Total project funding
  - DOE: $5,735 K
  - Contractor share: $410 K
- DOE Funding received in FY09
  - $1375 K
- Anticipated Total DOE Funding for FY10
  - $1735 K

Barriers addressed
- Durability
- Cost
- Electrode performance

Partners
- California Institute of Technology (Caltech)
  - W.A. Goddard, III, B. Merinov, Y. Sha, and T. Yu
- University of Illinois at Chicago (UIC)
  - J. Regalbuto, C. Cao, and H. Cho
- University of Nevada at Las Vegas (UNLV)
  - C. Heske, T. Hofmann, and Y. Zhang
- Oak Ridge National Laboratory (ORNL)
  - Karren More
- Los Alamos National Laboratory (LANL)
  - P. Zelenay, F. Garzon, H. Chung, and G. Wu
Relevance - Objectives

- Develop non-platinum cathode electrocatalysts for polymer electrolyte fuel cells to meet DOE targets that:
  - Promote the direct four-electron oxygen reduction reaction (ORR) with high electrocatalytic activity \(0.44 \text{ A/mg}_{\text{PGM}}; \, 720 \, \mu\text{A/cm}^2 \, @0.9 \, \text{V}_{\text{ir-free}}\)
  - Are chemically compatible with the acidic electrolyte and resistant to dissolution (<40% electrochemical area loss over 5000 h@\(\leq80^\circ\text{C}\) and 2000 h@\(>80^\circ\text{C}\))
  - Are low cost ($5/KW, 0.3 \, \text{mg PGM/cm}^2$)

- This year’s specific objectives:
  - Prepare/characterize model systems (bulk alloys) and nano-particles of Pd-Mo, Pd-Re, Pd-Ta, and Pd-W binaries and Pd-Cu-Mo, Pd-Cu-W, Pd-Cu-Re, Pd-Cu-Ta, and Pd-Cu-Ni ternaries:
    - Varying:
      - Pd to base metal ratio
      - Annealing temperature
      - Annealing atmosphere
    - Characterizing:
      - ORR activity
      - Surface composition
      - Electronic structure

- Impact:
  - Reduce cost by replacing Pt with less expensive noble metal/base metal alloys; expand pool of effective materials, which will reduce cost
  - Enhance noble stability by decreasing oxophilicity and oxidation-related degradation
  - Improve activity by modifying surface electronic properties
Approach

- **Bimetallic systems (base metal-noble metal)**
  - Surface skin of noble metal over noble metal-base metal alloy particle interior to form protective layer
  - Base metal component chosen to modify electronic properties of noble metal making it more “Pt-like”
  - Choice of bimetallic systems based on calculated “d-band center” shifts and surface segregation energies¹

<table>
<thead>
<tr>
<th>Solute Metal</th>
<th>Noble Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>75-75-75-75%</td>
<td>100-50-75-75%</td>
</tr>
</tbody>
</table>

“Surface Uniform” “Surface Segregated” Case

- **FY10 Milestone**
  Synthesize and evaluate the oxygen reduction activity, valence band structure, and stability of bulk electrodes and nano-particles of three palladium-base metal alloy systems
  - Fabricated/synthesized:
    - Bulk electrodes: 6 systems, 21 compositions
    - Nano-particles: 5 systems, 22 compositions

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Project approach/tasks

- **Computational studies (Caltech)**
  - Quantum mechanical and large scale molecular dynamics
  - Preferred catalyst structures
    - Surface segregation energies
  - Electronic structure
    - d-band centers/valence band structure
  - Reaction pathways and kinetics

- **Nano-particle synthesis on high-surface-area carbon support (Argonne, UIC)**
  - Co-impregnation
  - Colloidal
  - Strong-electrostatic adsorption

- **Model systems: bulk electrode fabrication and characterization (UNLV, Argonne)**
  - Thin films of one metal deposited on substrate of another metal
    - Deposition and annealing in UHV
  - Arc-melted foils and ingots
    - Annealed in UHV, Argon, H₂-containing atm.
  - ORR activity characterized in aqueous electrolyte
  - Surface composition and electronic structure (UHV-XPS)

- **Nano-particle characterization (Argonne, ORNL, UNLV, UIC)**
  - ORR activity and stability screening (rotating ring-disk technique)
  - Composition (XPS, XRD, EDAX, TEM)
  - Particle size/Morphology (TEM)
  - Electronic structure (UHV-XPS)

- **Membrane-electrode assembly fabrication and testing (LANL, ORNL)**
  - Performance and durability using accelerated test protocol
Accomplishments

Calculated ORR energetics for Pd and Rh Alloys

- Pd<sub>3</sub>W, Pd<sub>3</sub>Mo, Pd<sub>3</sub>Re, Pd<sub>3</sub>Ta, Rh<sub>3</sub>Co, Rh<sub>3</sub>Fe selected based on d-band center (close to that of Pt: -2.47 eV) and favorable energy for noble metal segregation (<-0.3 eV)

### Energies (eV)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>d-band (eV)</th>
<th>Segregation (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd&lt;sub&gt;3&lt;/sub&gt;W</td>
<td>-2.39</td>
<td>-1.99</td>
</tr>
<tr>
<td>Pd&lt;sub&gt;3&lt;/sub&gt;Mo</td>
<td>-2.25</td>
<td>-1.23</td>
</tr>
<tr>
<td>Pd&lt;sub&gt;3&lt;/sub&gt;Re</td>
<td>-2.28</td>
<td>-2.09</td>
</tr>
<tr>
<td>Pd&lt;sub&gt;3&lt;/sub&gt;Ta</td>
<td>-2.44</td>
<td>-0.33</td>
</tr>
<tr>
<td>Rh&lt;sub&gt;3&lt;/sub&gt;Co</td>
<td>-2.17</td>
<td>-0.77</td>
</tr>
<tr>
<td>Rh&lt;sub&gt;3&lt;/sub&gt;Fe</td>
<td>-2.10</td>
<td></td>
</tr>
</tbody>
</table>

### Binding Energy (eV)

<table>
<thead>
<tr>
<th></th>
<th>Pd</th>
<th>Pd&lt;sub&gt;3&lt;/sub&gt;Mo</th>
<th>Pd&lt;sub&gt;3&lt;/sub&gt;Re</th>
<th>Pd&lt;sub&gt;3&lt;/sub&gt;Ta</th>
<th>Pd&lt;sub&gt;3&lt;/sub&gt;W</th>
<th>Rh</th>
<th>Rh&lt;sub&gt;3&lt;/sub&gt;Co</th>
<th>Rh&lt;sub&gt;3&lt;/sub&gt;Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>M-H/H</td>
<td>-2.92</td>
<td>-2.63</td>
<td>-2.69</td>
<td>-2.59</td>
<td>-2.60</td>
<td>-2.97</td>
<td>-3.01</td>
<td>-3.05</td>
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<tr>
<td>M-O/O</td>
<td>-4.31</td>
<td>-4.05</td>
<td>-4.11</td>
<td>-4.02</td>
<td>-3.96</td>
<td>-5.12</td>
<td>-5.09</td>
<td>-5.10</td>
</tr>
<tr>
<td>M-HH/HH</td>
<td>0.04</td>
<td>0.15</td>
<td>0.08</td>
<td>0.15</td>
<td>0.17</td>
<td>0.08</td>
<td>-0.14</td>
<td>-0.10</td>
</tr>
<tr>
<td>M-O&lt;sub&gt;2&lt;/sub&gt;/O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-0.96</td>
<td>-0.74</td>
<td>-0.81</td>
<td>-0.67</td>
<td>-0.85</td>
<td>-1.63</td>
<td>-1.56</td>
<td>-1.55</td>
</tr>
<tr>
<td>M-OOH/OOH</td>
<td>-1.38</td>
<td>-1.51</td>
<td>-1.57</td>
<td>-1.49</td>
<td>-1.52</td>
<td>-1.92</td>
<td>-1.85</td>
<td>-1.88</td>
</tr>
<tr>
<td>M-H&lt;sub&gt;2&lt;/sub&gt;O/&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-0.63</td>
<td>-0.47</td>
<td>-0.55</td>
<td>-0.43</td>
<td>-0.50</td>
<td>-0.71</td>
<td>-0.75</td>
<td>-0.73</td>
</tr>
<tr>
<td>M-H&lt;sub&gt;2&lt;/sub&gt;O/H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>-0.55</td>
<td>-0.54</td>
<td>-0.60</td>
<td>-0.46</td>
<td>-0.56</td>
<td>-0.68</td>
<td>-0.61</td>
<td>-0.65</td>
</tr>
</tbody>
</table>

### Reaction Barriers

<table>
<thead>
<tr>
<th></th>
<th>Pd</th>
<th>Pd&lt;sub&gt;3&lt;/sub&gt;Mo</th>
<th>Pd&lt;sub&gt;3&lt;/sub&gt;Re</th>
<th>Pd&lt;sub&gt;3&lt;/sub&gt;Ta</th>
<th>Pd&lt;sub&gt;3&lt;/sub&gt;W</th>
<th>Rh</th>
<th>Rh&lt;sub&gt;3&lt;/sub&gt;Co</th>
<th>Rh&lt;sub&gt;3&lt;/sub&gt;Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt; Dissociation</td>
<td>0.00</td>
<td>0.09</td>
<td>0.00</td>
<td>0.01</td>
<td>0.14</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt; Dissociation</td>
<td>0.30</td>
<td>0.48</td>
<td>0.22</td>
<td>0.59</td>
<td>0.65</td>
<td>0.00</td>
<td>0.07</td>
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<tr>
<td>OH Formation</td>
<td>0.33</td>
<td>0.25</td>
<td>0.23</td>
<td>0.20</td>
<td>0.23</td>
<td>0.87</td>
<td>0.84</td>
<td>0.85</td>
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<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O Formation</td>
<td>0.77</td>
<td>0.69</td>
<td>0.69</td>
<td>0.73</td>
<td>0.68</td>
<td>0.80</td>
<td>0.73</td>
<td>0.94</td>
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<tr>
<td>OOH Formation</td>
<td>0.63</td>
<td>0.58</td>
<td>0.58</td>
<td>0.54</td>
<td>0.69</td>
<td>0.52</td>
<td>0.56</td>
<td>0.47</td>
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<tr>
<td>OOH Dissociation</td>
<td>0.00</td>
<td>0.03</td>
<td>0.11</td>
<td>0.00</td>
<td>0.01</td>
<td>0.03</td>
<td>0.00</td>
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<tr>
<td>H-OOH dissociation</td>
<td>0.00</td>
<td>0.23</td>
<td>0.31</td>
<td>0.13</td>
<td>0.26</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>O hydration</td>
<td>0.95</td>
<td>0.59</td>
<td>0.62</td>
<td>0.50</td>
<td>0.62</td>
<td>0.87</td>
<td>1.01</td>
<td>1.05</td>
</tr>
</tbody>
</table>

- Alloying Pd decreases barriers for H<sub>2</sub>O formation and O hydration (two key steps)
- Alloying Rh increases barriers for these steps
- Alloying Pd decreases binding energy of H, O, O<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub>; increases binding energy of OH, OOH, and H<sub>2</sub>O
- Alloying Rh increases binding energy of OH
Accomplishments

Calculated effect of solvent on ORR energetics

- **Pd and Pd alloys**
  - Reaction steps in gas phase: OOH formation, OOH dissociation, O hydration, HOH formation
  - Reaction steps in solvent: O₂ dissociation, OH formation, HOH formation
  - Activity predictions: Pd alloys have higher ORR activities than pure Pd

- **Rh and Rh alloys**
  - Reaction steps in gas phase: O₂ dissociation, O hydration, HOH formation
  - Reaction steps in solvent: O₂ dissociation, OH formation, HOH formation
  - Activity predictions: Rh₃Co has higher ORR activity than Rh, Rh₃Fe has lower activity than Rh

<table>
<thead>
<tr>
<th>Reaction Barriers</th>
<th>Pd</th>
<th>Pd₃Mo</th>
<th>Pd₃Re</th>
<th>Pd₃Ta</th>
<th>Pd₃W</th>
<th>Rh</th>
<th>Rh₃Co</th>
<th>Rh₃Fe</th>
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</thead>
<tbody>
<tr>
<td>O₂ Dissociation</td>
<td>0.77</td>
<td>1.08</td>
<td>0.70</td>
<td>1.26</td>
<td>1.18</td>
<td>0.14</td>
<td>0.29</td>
<td>0.13</td>
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<tr>
<td>OH Formation</td>
<td>0.19</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.60</td>
<td>0.49</td>
<td>0.61</td>
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<tr>
<td>H₂O Formation</td>
<td>0.55</td>
<td>0.53</td>
<td>0.56</td>
<td>0.51</td>
<td>0.52</td>
<td>0.74</td>
<td>0.73</td>
<td>0.88</td>
</tr>
<tr>
<td>OOH Formation</td>
<td>0.49</td>
<td>0.29</td>
<td>0.36</td>
<td>0.23</td>
<td>0.42</td>
<td>0.48</td>
<td>0.49</td>
<td>0.39</td>
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<tr>
<td>OOH Dissociation</td>
<td>0.29</td>
<td>0.28</td>
<td>0.30</td>
<td>0.38</td>
<td>0.30</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>O hydration</td>
<td>0.00</td>
<td>0.24</td>
<td>0.31</td>
<td>0.34</td>
<td>0.28</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>Overall Barriers</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>without solvent</td>
<td>0.55</td>
<td>0.53</td>
<td>0.56</td>
<td>0.51</td>
<td>0.52</td>
<td>0.74</td>
<td>0.73</td>
<td>0.88</td>
</tr>
<tr>
<td>with solvent</td>
<td>0.77</td>
<td>0.69</td>
<td>0.69</td>
<td>0.73</td>
<td>0.68</td>
<td>0.80</td>
<td>0.73</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Activity predictions are in qualitative agreement with trends in measured ORR activity: Pd>Rh; Pd alloyed with Mo, Re, or W > Pd

See Supplementary Section for details on Solvent Effect calculations
## Accommplishments

**Calculated effect of oxygen on surface segregation energies of select Pt and Pd alloys**

Only Pd$_3$Ir and Pd$_3$Os remain segregated in the presence of adsorbed oxygen

<table>
<thead>
<tr>
<th>Pt Alloy</th>
<th>Pure Metal Segregation Energy (eV)</th>
<th>Adsorbed Oxygen Segregation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$_3$Co</td>
<td>0.500</td>
<td>-0.620</td>
</tr>
<tr>
<td>Pt$_3$Ni</td>
<td>0.462</td>
<td>-0.616</td>
</tr>
<tr>
<td>Pd$_3$Au</td>
<td>-0.39</td>
<td>0.133</td>
</tr>
<tr>
<td>Pd$_3$Cu</td>
<td>0.031</td>
<td>-0.335</td>
</tr>
<tr>
<td>Pd$_3$Ir</td>
<td>0.764</td>
<td>0.119</td>
</tr>
<tr>
<td>Pd$_3$Mo</td>
<td>1.232</td>
<td>-1.407</td>
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<tr>
<td>Pd$_3$Os</td>
<td>1.275</td>
<td>0.090</td>
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<tr>
<td>Pd$_3$Re</td>
<td>2.089</td>
<td>-0.867</td>
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<tr>
<td>Pd$_3$Rh</td>
<td>0.474</td>
<td>-0.135</td>
</tr>
<tr>
<td>Pd$_3$Ru</td>
<td>0.884</td>
<td>-1.481</td>
</tr>
<tr>
<td>Pd$_3$Ta</td>
<td>0.334</td>
<td>-3.831</td>
</tr>
<tr>
<td>Pd$_3$W</td>
<td>1.996</td>
<td>-2.072</td>
</tr>
</tbody>
</table>

- Only Pd$_3$Ir and Pd$_3$Os segregate in both pure metal case and in the presence of adsorbed O
- Pd$_3$Mo, Pd$_3$Re, Pd$_3$Ta, and Pd$_3$W are extremely non-segregating in presence of O
### Summary of model and nano-particle systems studied

<table>
<thead>
<tr>
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</tr>
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<tbody>
<tr>
<td><strong>PGM loading (wt%)</strong></td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>11-20</td>
<td>4-15</td>
<td>20-27</td>
<td>2-4</td>
<td>7-11</td>
</tr>
<tr>
<td><strong>Pd precursor</strong></td>
<td>Metal</td>
<td>Metal</td>
<td>Metal</td>
<td>Metal</td>
<td>Metal</td>
<td>Metal</td>
<td>Metal</td>
<td>Metal</td>
<td>OAc</td>
<td>Chloride</td>
<td>Acac, Amine</td>
<td>Acac, Amine</td>
<td>Acetate</td>
</tr>
<tr>
<td><strong>BM precursor</strong></td>
<td>Metal</td>
<td>Metal</td>
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<td>Metal</td>
<td>Metal</td>
<td>Metal</td>
<td>n/a</td>
<td>n/a</td>
<td>OAc</td>
<td>Perrhenic acid</td>
<td>Carbonyl, Ammonium molybdate</td>
<td>Carbonyl, Ammonium tungstate</td>
<td>Cu chloride, Ni nitrate</td>
</tr>
<tr>
<td><strong>Annealing/Post-deposition heat treatment temperature (°C)</strong></td>
<td>RT-800</td>
<td>RT-1345</td>
<td>RT-1420</td>
<td>RT-1200</td>
<td>RT-1340</td>
<td>RT-800</td>
<td>RT-1000</td>
<td>1050</td>
<td>350-550</td>
<td>300/1 h &amp; 450/2 h</td>
<td>700</td>
<td>400</td>
<td>500-800</td>
</tr>
<tr>
<td><strong>Heat treatment atmosphere</strong></td>
<td>Ar, 100 ppm H₂ in Ar, 1% H₂ in Ar, 3.5-3.7% H₂ in He</td>
<td>100% H₂</td>
<td>100% H₂</td>
<td>100% H₂</td>
<td>He &amp; H₂</td>
<td>3.5% H₂</td>
<td>He &amp; H₂</td>
<td>3.9% H₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Accomplishments

Evaluated relative ORR activity of annealed model systems

- Model systems: arc-melted ingots of 5 mm dia x 4 mm thick
- All ingots tested in 0.1 M HClO₄ quiescent solution in meniscus configuration
  - Before annealing and after annealing in O₂-saturated and Ar-purged electrolyte
- Select ingots are being evaluated in RDE configuration
- Annealing atmospheres: 3.5-3.7%H₂/He, 1% H₂/Ar, 100 ppm H₂/Ar, and Ar
- Annealing temperature: 600 - 1500°C
Accomplishments

Evaluated relative ORR activity of annealed Pd alloy ingots

- **Annealing Pd alloys promotes surface segregation of Pd**
  - Evidenced by improved ORR activity and Pd-like voltammetry
  - Degree of Pd segregation depends on annealing environment and temperature, oxophilicity of base metal, and Pd:BM ratio
    - Annealing in Ar promotes base metal oxide formation
    - Annealing in H₂-containing environment can result in hydride
    - Careful control of annealing environment is necessary

- **Pd-Mo (72-28) shows highest enhancement of ORR activity**
  - $E_{p/2}$ increased by 22 mV compared to Pd
  - $E_{p/2}$ 28 mV lower than that of Pt

<table>
<thead>
<tr>
<th>System (Pd:BM mole ratio)</th>
<th>Annealing conditions for Max. ORR activity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp (°C)/atm</td>
</tr>
<tr>
<td>Pt</td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>926, Ar</td>
</tr>
<tr>
<td>Pd-Ta (98:2)</td>
<td>600, Ar</td>
</tr>
<tr>
<td>Pd-Ta (95:5)</td>
<td>720, 100 ppm H₂/Ar</td>
</tr>
<tr>
<td>Pd-Re (95:5)</td>
<td>620, Ar alt. w/ 100 ppm H₂/Ar</td>
</tr>
<tr>
<td>Pd-Mo (75:25)</td>
<td>100 ppm H₂/Ar</td>
</tr>
<tr>
<td>Pd-Mo (90:10)</td>
<td>650, 100 ppm H₂/Ar</td>
</tr>
<tr>
<td>Pd-Mo (72:28)</td>
<td>1050, 1% H₂/Ar and Ar alternately</td>
</tr>
<tr>
<td>Pd-Mo (53:47)</td>
<td>1420, 1% H₂/Ar</td>
</tr>
<tr>
<td>Pd-W (80:20)</td>
<td>930, 100 ppm H₂/Ar</td>
</tr>
<tr>
<td>Pd-W (75:25)</td>
<td>1010, 1% H₂</td>
</tr>
<tr>
<td>Pd-Cu (75:25)</td>
<td>500, Ar</td>
</tr>
<tr>
<td>Pd-Cu (50:50)</td>
<td>560, 3.5% H₂/He</td>
</tr>
<tr>
<td>Pd-Cu (33:67)</td>
<td>580, 3.5% H₂/He</td>
</tr>
<tr>
<td>Pd-Cu (25:75)</td>
<td>550, 3.5% H₂/He</td>
</tr>
<tr>
<td>Pt</td>
<td>1050, Ar</td>
</tr>
</tbody>
</table>
Correlation of ORR activity and calculated d-band center

- Pd₃Mo shows 2.1x ORR activity enhancement over Pd
- However, Pd₃Mo activity still 2.6x below that of Pt
- Have we reached the top of the “volcano” curve?

**Calculated from measured E_p/2 at 50 mV/s using 68 mV/dec Tafel Slope**

*Note: Pd₃Ta and Pd₃Re have low ORR activity and Re or Ta oxide-like voltammetry*
Accomplishments

*Characterized valence band of PdMo model system*

- Mo modifies Pd valence band, extending density of states (DOS) to higher binding energies
- $\text{Pd}_{75}\text{Mo}_{25}$ valence band is broader than $\text{Pd}_{x}\text{Cu}_{y}$ valence band
- Compared to Pt, PdMo and PdCu lack DOS near $E_F$ and at $>4 \text{ eV}$
- Need to know not just overall d-band center energy, but also
  - contributions of various states to valence band structure
  - involvement of these states in ORR

- $\text{Pd}_{75}\text{Mo}_{25}$ alloy annealed in UHV from 300 to 700 $^\circ$C
Accomplishments

*Synthesized nano-particles in three new Pd bimetallic systems*

- Techniques
  - Co-impregnation (Argonne)
  - Single-phase colloidal (Argonne)
  - Strong electrostatic adsorption (SEA) (UIC)

- Heat treatment in reducing atmosphere to form alloy, reduce precursors, remove capping agents

**Colloidal Synthesis**

\[ \text{Pd(acac)}_2 \quad \text{Mo(CO)}_6 \quad \text{Diphenyl ether} \]

\[ \text{245°C} \quad \text{Refluxed for 2 hrs under Ar} \]

\[ \text{Pd-Mo} \quad \text{(unsupported particles)} \]

**Strong-electrostatic adsorption**

- Vulcan, PZC = 8.9
- \(\text{MoO}_x\) or \(\text{WO}_x\), PZC = 2.2~4.0

\[ [\text{PdNH}_4]^2+ \]

- Impregnate at a pH in between PZCs for selective adsorption

\[ \text{Pd(acac)}_2 \quad \text{W(CO)}_6 \quad \text{O-xylene} \]

\[ \text{135-144°C} \quad \text{Refluxed for ≥ 15 hrs} \]

\[ \text{Capped Pd-W dispersed in hexane, stable (no settling) for extended time} \]
**Accomplishments**

**Characterized ORR activity of nano-particles of three bimetallic systems**

<table>
<thead>
<tr>
<th>System</th>
<th>Pd:BM (at. ratio)</th>
<th>Tech.</th>
<th>XRD/XPS/EDAX</th>
<th>Particle size (nm)</th>
<th>$i_m@0.8\text{ V (mA/mg Pd)}$</th>
<th>$i_s@0.8\text{ V (µA/cm}^2\text{)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-W</td>
<td>75:25, 50:50</td>
<td>Colloidal</td>
<td>• Alloys formed, WO$_x$ and Pd present on surface, no WO$_x$</td>
<td>9-11</td>
<td>93 (75:25@800°C)</td>
<td>830 (75:25@700°C)</td>
</tr>
<tr>
<td></td>
<td>8:90, 15:85, 26:74</td>
<td>SEA</td>
<td>• Pd selectively adsorbed on WO$_x$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd-Mo</td>
<td>90:10, 72:28, 55:45</td>
<td>Colloidal</td>
<td>• Alloy and carbide</td>
<td>5-20</td>
<td>138 (55:45@700°C)</td>
<td>600 (55:45@700°C)</td>
</tr>
<tr>
<td></td>
<td>10:90, 14:76, 18:82, 26:74</td>
<td>SEA</td>
<td>• Pd selectively adsorbed on MoO$_x$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd-Re</td>
<td>95:5, 75:25, 50:50, 33:67, 25:75</td>
<td>Co-Impl.</td>
<td>• Alloys formed</td>
<td>10-20</td>
<td>150 (3:1@300/450°C)</td>
<td>820 (1:1@ 300,450°C)</td>
</tr>
<tr>
<td>Pd-Ni-Cu</td>
<td>18:18:64</td>
<td>Colloidal</td>
<td>• Alloy formed, no free Cu or Ni</td>
<td>10-20</td>
<td>680 (550°C)</td>
<td>nd</td>
</tr>
<tr>
<td>Pd</td>
<td>100</td>
<td>E-Tek</td>
<td>• n/a</td>
<td>10</td>
<td>200</td>
<td>nd</td>
</tr>
</tbody>
</table>

- Base metal oxides present on nano-particle surfaces, blocking ORR

![Image of ORR activity and TEM images](image-url)
Collaborations

- **Project team (subs) within DOE H₂ Program**
  - California Institute of Technology (Caltech)
    - W.A. Goddard, III, B. Merinov, Y. Sha, and T. Yu
  - University of Illinois at Chicago (UIC)
    - J. Regalbuto, C. Cao, and H. Cho
  - University of Nevada at Las Vegas (UNLV)
    - C. Heske, T. Hofmann, and Y. Zhang
  - Oak Ridge National Laboratory (ORNL)
    - Karren More
  - Los Alamos National Laboratory (LANL)
    - P. Zelenay, F. Garzon, H. Chung, and G. Wu

- **Collaborators outside of DOE H₂ Program**
  - Caltech collaborates with Dr. Pezhman Shirvanian (Ford Motor Company) on computational modeling of advanced Pt-based cathode catalysts and supports.
  - UNLV collaborates with the groups of Marcus Bär (Helmholtz-Zentrum Berlin for Materials and Energy) and Lothar Weinhardt (U of Würzburg, Germany) on synchrotron studies at the Advanced Light Source.
Proposed Future Work

- Perform RDE studies on bi- and tri-metallic model systems (ingots) showing highest ORR activities
- Determine surface composition and valence band structure as a function of annealing temperature and atmosphere, using XPS, for these model systems
- Continue synthesis of nano-particles of most promising compositions identified in model system and computational studies, with goal of achieving base metal oxide-free surfaces
- Expand surface segregation calculations to include other noble metal:base metal ratios, ternaries, and effect of annealing atmosphere
- Study segregation effect for binary and ternary systems in the presence of different adsorbed species on the surface
- Study ternary systems, such as Pd-Cu-Mo, Pd-Cu-W, Pd-Cu-Re, Pd-Cu-Ta, Pd-Cu-Ni with varying Pd to base metal ratios to enhance activity and stability of highest activity binary system identified to date
- Continue determining alloy electronic structures using density of states (DOS) spectra and performing detailed analysis how the electronic structures affect the ORR activity
Summary

Relevance:
- Reduce the cost of polymer electrolyte fuel cell oxygen reduction catalysts by replacing Pt with alternative noble metals and less expensive base metals.

Approach:
- Bi- and tri-metallic non-Pt noble metal-base metal alloys favoring surface segregation of noble metal; modification of noble metal energetics by base metal to be Pt-like.

Accomplishments:
- Calculated ORR energetics for Pd and Rh alloys and effect of solvent on these energetics
- Calculated effect of adsorbed oxygen on surface segregation energies of Pt and Pd alloys
- Determined the effect of annealing temp. and atm. on the ORR activity of twenty-one bimetallic and trimetallic Pd bulk electrodes; best ORR activity enhancement with alloying was 2.1x (Pd₃Mo)
- Determined valence band structure of highest activity Pd alloys (Mo and Cu)

Collaboration:
- Project team of Caltech, UNLV, UIC, LANL, and ORNL
- Caltech collaborates with Ford Motor Company on computational studies of Pt-based cathode catalysts and supports.
- UNLV collaborates with Helmholtz-Zentrum Berlin for Materials and Energy and U of Würzburg, Germany on synchrotron studies.

Future Work:
- RDE studies and valence band characterization as a function of annealing temp. and atm. of bi- and tri-metallic Pd systems showing highest ORR activity
- Explore alternative nano-particle synthesis techniques to avoid formation of base metal oxide on surface
- Calculate and determine the electronic structure, surface segregation, and ORR activity for ternary systems to enhance the activity and stability of highest activity binary systems
Supplemental Slides
Solvent effect calculation details

(for results shown on slide 7)

- Employed Poisson-Boltzmann implicit solvent method as it is implemented in the Adaptive Poisson-Boltzmann Solver (APBS) which is incorporated in the Computational Materials Design Facility (CMDF) developed in the Materials and Process Simulation Center (MSC) at Caltech.

- The contributions of solvent and ions are considered through their electrostatic interactions with the solutes. The use of a continuum solvent environment leads to a consistent model for estimating the contribution of the solvent all along the reaction surface.
**Palladium-Copper model systems and nano-particles**

**Exposure to 0.6M HClO₄ for 3 days**

- ORR activity of Pd is enhanced by addition of Cu
  - ~2x for the 1:3 Pd:Cu
  - ~3x for the 1:1 Pd:Cu

**ORR activity in 0.1 M HClO₄**

- Before and After Acid Treatment

**Observations**

- Both Pd and Cu leach out, with preferential leaching of Cu
- **1:3 Pd:Cu**
  - Higher loss of both Pd and Cu than 1:1
  - Cu loss accompanied by loss of contracted lattice spacing
- **1:1 Pd:Cu**
  - Lower relative loss of Pd and Cu
  - Contracted lattice spacing retained
Palladium-Copper system
Comparison of measured and theoretical valence band structure

- Investigation of the electronic structure of alloys (collaborative work between Caltech and UNLV)
- Comparison of measured valence band for alloy foils at room temperature and after annealing with calculated ordered and disorder density of states
- Good agreement between theory and experiments can be achieved
  - Contributions from particular orbitals to density of states can be identified
  - Link to ORR kinetics can be established through calculations of energetics of ORR and electrochemical testing
- Disorder-order transition may occur for alloy foils above a threshold temperature
  - Possibility to establish a core-shell structure for nano-particle catalysts
Palladium-Copper thin film model systems

*Measurement of valence band structure*

- Thin Cu films have been deposited on Pd foils (and vice versa), followed by annealing in ultra-high vacuum and measurement of valence band density of states.
- At room temperature no alloying takes place, electronic structure = superposition of “independent” Pd and Cu states.
- Pd diffuses into Cu lattice at elevated temperatures and vice versa.
- Valence band structure shows alloying behavior.
- Electronic structure of catalyst surface can be tailored.
- Tailoring can be monitored by valence band XPS.

![Diagram showing XPS data and temperature effects on Pd/Cu and Cu/Pd systems.](image-url)