Development of High Temperature Membranes and Improved Cathode Catalysts

DOE contract DE-FC04C-02-Al-67608
2003 DOE Funds: 2.7 M$

DOE Merit Review

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UTC Fuel Cells

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Outline

• Objectives
• Approach
• Project timeline
• Technical highlights:
  – High-temperature membrane (HTM)
  – Advanced cathode catalysts
• Future work
Objectives and Approach

- **High temperature proton exchange membranes**
  - Develop membranes capable of satisfying DOE targets. Operating conditions: $120^\circ$C - $150^\circ$C and 1.0-1.5 atm.
  - Collaboration with leading polymer chemists to develop new membrane systems.

- **Advanced cathode catalysts**
  - Develop high concentration Pt-alloy catalyst systems with improved activity.
  - Utilize the higher activity, reduce catalyst-layer thickness and achieve reduced precious-metal loading (DOE goal of 0.05 mg/cm$^2$).
### Program Timeline

<table>
<thead>
<tr>
<th>Task</th>
<th>Task Description</th>
<th>2002</th>
<th>2003</th>
<th>2004</th>
<th>2005</th>
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<tbody>
<tr>
<td><strong>Phase 1</strong></td>
<td><strong>Catalyst Development</strong></td>
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<td><strong>1.1</strong></td>
<td>Catalyst Modeling</td>
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<td>Catalyst Characterization</td>
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<td><strong>Membrane Chemistry</strong></td>
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<td><strong>MEA Development &amp; Testing</strong></td>
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<td>Sub-Scale High Temperature MEA Fabrication</td>
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<td>MEA Optimization and Selection</td>
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<td><strong>Phase 3</strong></td>
<td><strong>Stack Demonstration</strong></td>
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<td>Stack Testing and Demonstration</td>
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<td><strong>Quarter from Start</strong></td>
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<td><strong>Phase 1</strong></td>
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<td><strong>Phase 2</strong></td>
<td>13</td>
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</table>

### Legend
- Green triangle: Task start
- Orange triangle: Task end
## Milestone Schedule

<table>
<thead>
<tr>
<th>PHASE</th>
<th>MILESTONE #</th>
<th>MILESTONE</th>
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<tbody>
<tr>
<td><strong>Phase 1</strong></td>
<td>1</td>
<td>Preliminary model completed</td>
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<tr>
<td>Membrane Chemistry</td>
<td>2</td>
<td>Begin alloy synthesis</td>
</tr>
<tr>
<td>and Catalyst Development</td>
<td>3</td>
<td>Complete alloy synthesis</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>Complete characterization and down-selection</td>
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<tr>
<td></td>
<td>5</td>
<td>Complete modeling + correlation</td>
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<tr>
<td></td>
<td>6</td>
<td>Membrane specification to team members</td>
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<tr>
<td></td>
<td>7</td>
<td>Initial sample membrane</td>
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<tr>
<td></td>
<td>8</td>
<td>Characterization of initial membrane samples</td>
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<tr>
<td></td>
<td>9</td>
<td>Synthesis of final membrane samples</td>
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<tr>
<td></td>
<td>10</td>
<td>Select membrane for Phase 2</td>
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<tr>
<td><strong>Phase 2</strong></td>
<td>11a</td>
<td>Initial electrode fabrication (catalyst)</td>
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<tr>
<td>MEA Development and Testing</td>
<td>11b</td>
<td>Initial electrode fabrication (HTM)</td>
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<tr>
<td></td>
<td>12</td>
<td>Complete subscale testing for cathode catalyst and down-select catalysts</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>Complete subscale testing for membranes and down-select membrane(s)</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>Select optimum catalyst-membrane combination for Phase 3</td>
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<tr>
<td><strong>Phase 3</strong></td>
<td>15</td>
<td>Complete test and assembly of 2-20 cell stacks.</td>
</tr>
<tr>
<td>Stack Demonstration</td>
<td>16</td>
<td>Complete stack verification test</td>
</tr>
</tbody>
</table>
High-Temperature Membrane Team

- Collaboration with leading polymer chemists to develop new membrane systems.
- Systems include non-Nafion® and also modified-Nafion® membranes.
Advanced Cathode Catalyst Team

- Collaboration with leading electrochemists to develop higher activity catalyst systems.
- Systems include binary and ternary Pt alloys.
- Various deposition routes being investigated.
High-Temperature Membranes
Summary of Technical Achievements

- 4 membrane systems with proton conductivity on the order of 10 mS/cm at 120 C and 50% RH synthesized.
  - BPSH from Va. Tech
  - Modified S-PEEK from SRI
  - FPES from Penn State and
  - HPA filled Nafion® from IONOMEM
- Majority of membranes synthesized date on the program require hydrophilic fillers to conduct at reduced RH.
- IONOMEM has established a baseline for HTM performance of 0.6 V at 0.4 A/cm² (120 C, 30% RH).
System Pressure Requirements

System P vs. RH vs. T

- 100% Relative Humidity (Inlet)
- 50% Relative Humidity (Inlet)
- 35% Relative Humidity (Inlet)

Constant $p(O_2)=0.063$
SRI Approach

- SRI polymer membrane is based on sulfonated liquid crystalline polymers crosslinked to produce dimensionally stable and flexible membranes.

- Hydrophilic polymers designed to retain water of hydration are added to the membrane to aid in conductivity at reduced RH.
Membrane Conductivity at 120ºC vs. RH

- Conductivity of 0.011 S/cm at 120ºC@ 30% relative humidity and 0.038 S/cm at 120ºC@ 47% relative humidity.
F-PES Membrane (Penn State)

1. Conductivity (S/cm) vs. Relative Humidity (%)
   - Nafion 117
   - FPES II-1 (10 eq)
   - FPES II-2 (15 eq)
   - FPES II-2 (20 eq)

2. Water Uptake (wt%) vs. Relative Humidity (%)
   - Nafion 117
   - FPES II-1 (10 eq)
   - FPES II-2 (20 eq)

3. Molecular structure of F-PES membrane
BPSH Membrane Virginia Tech

Upper use temperature fully - hydrated $T_g$
- N117: 99°C
- BPSH-35: 135°C
- 15% ZrP BPSH-35
- 30% HPA BPSH-35

Conductivity (mS/cm)
- N117: 40 mS/cm
- BPSH-35: 5 mS/cm
- 15% ZrP BPSH-35: 5 mS/cm
- 30% HPA BPSH-35: 10 mS/cm

Upper use temperature: 120°C
45% RH

Bi-phenyl sulfones

Hydrophobic

Hydrophilic

0.2 ohm-cm² [Spec. 0.1 ohm-cm²]
Nafion®-HPA Composite Membranes (IONOMEM)

Nafion®-Teflon®-phosphotungstic acid (HPA)

80 °C; 400 mA/cm² at 0.7 V

120 °C; 400 mA/cm² at 0.6 V

80 °C and 120 °C, 1.0 atm.

H₂/air reactants

3.3/4.0 Stoich.
Future Work (2003)

• Further optimization of membrane systems and/or fillers required to improve conductivity at practical RH.
• Develop a generalized stability template for HTMs.
• Initiate HTM down-select process.
• Initiate HTMEA fabrication and optimization.
Advanced Cathode Catalyst
Summary of Technical Achievements

- Slab band calculations using VASP program have provided insight into binary alloy skin effect.
- Higher activity and more stable binary Pt alloys synthesized using the colloidal-sol, carbothermal, and pulse electrodeposition routes.
- Reproducible and SOA CCMs fabricated using the decal transfer process.
**VASP Modeling (Case Western)**

\[ \Delta U^o = U^o(\text{alloy}) - U^o(\text{Pt}) = \]
\[ [ (D_0(\text{OH})_\text{Pt} - D_0(\text{OH}_2)_\text{Pt} ) - [D_0(\text{OH})_{\text{alloy}} - D_0(\text{OH}_2)_{\text{alloy}} ] \]

<table>
<thead>
<tr>
<th>Catalyst surface</th>
<th>(D_0(\text{Surface-OH})) eV</th>
<th>(D_0(\text{Surface-OH}_2)) eV</th>
<th>(\Delta U^o) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(111) ((\theta = 0 \text{ ML}))</td>
<td>2.371</td>
<td>0.231</td>
<td>0</td>
</tr>
<tr>
<td>Pt(111)-skin on Pt(_3)Cr ((\theta = 0 \text{ ML}))</td>
<td>2.241</td>
<td>0.210</td>
<td>0.11</td>
</tr>
<tr>
<td>Pt(_3)Cr mixed metal surface ((\theta =0 \text{ ML}))</td>
<td>3.316 on Cr</td>
<td>0.628 on Cr</td>
<td>-0.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.516 on Pt</td>
<td>-0.17</td>
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</table>

- On Pt-skin, model model predicts that charge transfers from Cr to Pt skin.
Shell-Core Structures (UTCFC)

- The model studies support the following model structures for composite catalysts based on the work-function differences.
- Current effort is focused on verifying this core-shell concept experimentally in conjunction with the theoretical modeling.

![Graph showing work function difference for various elements compared to Pt.]
Kinetic Enhancement with Pt-Co Binary Alloy (UTCFC)

- True catalyst activity of Pt-Co is approximately 2.2 X Pt.

![Graph showing overpotential vs. current density with Tafel Slope ~70mV/decade and a ratio of vol. exchange current densities ~1.25.]

\[ \eta = A + B \log(i) \]

\[ i = p_{O_2} a i_0 e^{-\frac{F}{RT} \eta} \]

Air and H\textsubscript{2}: Low Stoich.
T=65°C
Initial performance
Subscale cell
40 wt% Pt
Cycling Stability with Pt-Co

(a) PtCo CCM

4000 Cycles
1.3 V-0.9 V

- The electron microprobe analysis shows no evidence of Co in the membrane and/or anode.
- The absence of Co migration is a strong benefit for the Pt/Co alloy system.
Pt Pulse Electrodeposition (USC)

Pt wt% vs. Surface area vs. Deposition Charge

Sample Performance Curve

- ETEK commercial electrode
- Pulse deposition by USC

USC (0.15mg/cm² of Pt)
ETEK (0.4mg/cm² of Pt)
Nafion 112
Cell Temperature: 75 °C
H₂/O₂ (flow rate: 1.5/2 stoichiometric)
Pressure: 1atm
CCM Fabrication (UTRC)

- Reproducible and SOA CCMs currently being fabricated with decal transfer process.

<table>
<thead>
<tr>
<th>CCM ID</th>
<th>V, mV @ 400 mA/cm H₂/O₂</th>
<th>V, mV @ 400 mA/cm H₂/Air</th>
<th>V, mV @ 100 mA/cm H₂/O₂</th>
<th>V, mV @ 100 mA/cm H₂/Air</th>
</tr>
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<tbody>
<tr>
<td>DOE target**</td>
<td>0.80</td>
<td>0.85</td>
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<tr>
<td>PEM 411***</td>
<td>0.824</td>
<td>0.786</td>
<td>0.885</td>
<td>0.857</td>
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<td>PEM 404</td>
<td>0.800</td>
<td>0.760</td>
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<td>PEM 413</td>
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<td>PEM 414</td>
<td>0.790</td>
<td>0.748</td>
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<td>0.857</td>
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<td>PEM 415</td>
<td>0.810</td>
<td>0.767</td>
<td>0.887</td>
<td>0.854</td>
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<tr>
<td>PEM 416</td>
<td>0.798</td>
<td>0.756</td>
<td>0.886</td>
<td>0.854</td>
</tr>
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</table>

** DOE targets are specified for 85%H₂/60%O₂ utilization;
*** Pt Loading on cathode side=0.4g/cm²;
Future Work (2003)

• Investigate the feasibility of Pt/X skin effect.
• Continue Pt-alloy synthesis using the various routes and optimize for activity and stability.
• Initiate catalyst down-select process.
• Investigate several methodologies to reduce Pt loading (e.g., ionomer gradient, etc.)