Tungsten Cathode Catalyst for PEM Cells

2006 DOE Hydrogen, Fuel Cells Infrastructure Technologies Program Review

Joel Christian, Robert Mendenhall, Sean Smith, Richard Gingerich, Hans-Joachim Lunk, Tuan Dang

OSRAM SYLVANIA Products Inc.

May 17, 2006

Project ID# FCP 40

This presentation does not contain any proprietary or confidential information
Overview

Timeline
Project Start: Feb. 1, 2005
Project End: July 1, 2006
Percent Complete: 90%

Budget
Project: $406,250
- DOE Share: $325,000
- Contractor: $81,250
Funding in ‘05: $283,236

Technical Barriers/Targets
Non-Pt Catalyst Activity
• > 130 A/cm³ @ 0.8V
Durability
• 5000 hours (cycling)
Cost
• < 8 $/kW

Partners
LANL — testing and ink formulation
Objectives

Perform R&D on tungsten electrocatalysts to improve power output per gram of material from baseline. This includes evaluating current catalyst in cathode application, and optimizing catalyst synthesis to achieve activity improvement towards attaining the DOE technical targets for non-platinum catalysts. Performance evaluation at 250 hours, and over 1000 hours.

The goal of this work is to produce a catalyst with high specific power at a cost significantly lower than platinum.
Approach

• Employ reduced polytungstates as cathode electrocatalysts

• Seek performance improvements by optimizing:
  – precursor composition
  – precursor loading on carbon
  – ink formulation
  – activation conditions

• Perform electrochemical tests for performance and lifetime
Technical Accomplishments

• Established catalysis in rotating disk half-cell
• Demonstrated catalyst improvement
  – At LANL
    • comparing 2004 and 2005 materials, W|Pt 5cm² cell
    • exceeded project milestone by 50% to 0.02 A/cm²
      – at 0.24V, during 20 hr life test
  – Internal testing
    • 4-fold improvement to 0.035 A/cm² at 0.24V
    • demonstrated catalyst life to 3200hrs
Technical Accomplishments

• Completed work in 5 key tasks:
  – activation conditions
  – precursor composition
  – precursor loading on carbon
  – ink formulation
  – analysis

• Composition change provided the increase in cathode performance
Tungsten Only Cell — RDE (anode and cathode)

Activated POM on XC-72
Type IV - RDE "C" - 5mm GC disk

Conditions:
0.5 M HClO4
5 mV/sec
2000 RPM
CE: Carbon Rod
RE: SCE (Hg/Ag)
WE: Thin film on Glassy Carbon

Demonstration of Catalytic Activity

2006 DOE Annual Review
Tungsten Only Cell — RDE

XPS Analysis of RDE Surface

- platinum undetected
- XPS shows reduced W(IV) present
Project Results – LANL Testing

Activity Improved to 0.078 A/cm²
Project Results – LANL Testing

2004

20 hour life test at 0.24V shows 2.5x improvement to 0.02 A/cm²

2005

both tests at 0.24V, 5cm² cell
2004 Test: ~0.04 A in cell = 0.008 A/cm²
2005 Test: 0.1 A in cell = 0.02 A/cm²
This comparison shows an improvement of 2.5x, project milestone was 2x

OSRAM-SYLVANIA Cathode Catalyst Testing

Short Life Test

Anode: 0.20 mgPt/cm²; Cathode: 0.39 mgW/cm²
MEA Cell Area: 5 cm²; Membrane: Nafion 112; Tcell: 80°C; Pressure: 30 psig
H₂/Air Flow: 160/550 sccm
Project Results – Current Output at 2000 hrs

Volumetric current density at 0.8V exceeds DOE non-precious status

60°C, H₂:Air, without iR correction, test at OSRAM SYLVANIA

2006 DOE Annual Review
Project Results - Life

No Degradation in Cell Performance to 3200 Hours

H₂:Air, initially RT then 60°C
Accomplishments – Activation Task

Cyclic Voltammogram of Na$_6$[H$_2$W$_{12}$O$_{40}$] precursor

Potential (Volts vs SCE)

Current (mA)

50 mV/sec

Current Pathway for Metatungstate

Source: Launay, JINC 38, 807 (1976)

W – W
3.3 Å
+ 6 e-
re-arrangement changes geometry

W – W
2.5 Å

reduced POM

Source: Jeannin, IC 1980 p 2933

2006 DOE Annual Review
Precursor loading on carbon

- Carbon Analysis:
  - PZC (isoelectric point)
  - pore size
- Objective:
  - optimizing of W loading on C

Pore Size Distribution of XC-72
Future Work

POM has a higher possible site density (SD) than Pt

Idealized polytungstate and Pt electrode surfaces

16 (10^{20}\text{sites/cm}^3) 75\% Metal Utilization

7.6 (10^{20}\text{sites/cm}^3) 5\% Metal Utilization
## Tungsten catalyst on track to meet the 2010 targets

<table>
<thead>
<tr>
<th>Mat’l</th>
<th>TOF</th>
<th>SD</th>
<th>SD_{MAX}</th>
<th>A/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(2)</td>
<td>25</td>
<td>3.2</td>
<td>7.6^{(1,4)}</td>
<td>1300</td>
</tr>
<tr>
<td>W—POM (current)</td>
<td>1.59</td>
<td>0.62</td>
<td>16^{(4)}</td>
<td>16</td>
</tr>
<tr>
<td>2010 POM</td>
<td>2</td>
<td>4.2</td>
<td>6.77x</td>
<td>136</td>
</tr>
<tr>
<td>POM_{MAX}</td>
<td>5</td>
<td>16</td>
<td></td>
<td>1300</td>
</tr>
<tr>
<td>req’d³</td>
<td>1.6-4</td>
<td>3.1</td>
<td></td>
<td>60 - 160</td>
</tr>
</tbody>
</table>

TOF = turnover frequency  
(catalytic reactions per second per site)

SD = site density  
(10^{20} catalytic sites per cm³)

---

*ref 1:* Fuel Cell Handbook v2 p 471, citing Kinoshita  
*ref 2:* Gasteiger et al, Appl Cat B 56 (2005) 9-35  
*ref 3:* Wagner et al, DOE Workshop 3/20/03  
*ref 4:* lecture notes, Jim Benushi, Cabot Corp.
Areas for Improvement

Charge Transfer Kinetics (TOF)

Active Sites (SD)

Compositional Changes (TOF, SD)

Stability Enhancement (TOF, SD)

Redox Tuning (TOF, SD)
Future Work

• Project conclusion
  – complete data collection
  – final report by 6/30/06

• Proposed for FY07
  – Continuing investigation on:
    • demonstration of activity (in a Pt-free cell)
    • optimization of activation step
    • precursor composition
    • methods to improve loading/dispersion

• Proposed multi-year program FY07/FY10
  – meet 2010 DOE target of 130 A/cm³
Summary

• Catalysis demonstrated on rotated disk electrode
  – anode and cathode catalysis

• PEM Cell performance demonstrated
  – above DOE’s non-precious metal 2004 status
  – cathode operation to 3200 hours
  – project milestone exceeded

• Space model shows on-track to 2010 target
  – plan proposed to achieve 130 A/cm³
Backup Slides
Critical Assumptions and Issues

• Adventitious Platinum
  – Pt could migrate across membrane during
    • synthesis/activation
    • operation
  – Protocol is needed to assess effect in PEM cell
    • detection of Pt in non-Pt catalyst area
    • quantification of Pt in non-Pt catalyst area
    • performance effect of Pt in non-Pt catalyst area
  – Life test MEA assumes no Pt
    • analysis protocol being developed
Acid Resistant Elements

![Periodic Table of Elements]

2006 DOE Annual Review
Polyoxometalate (POM) - Features

- Keggin type shown
- One central heteroatom
- Octahedra of WO$_6$ “poly” atoms
- Substituted “poly” atoms
  - Poly- W, Mo, V, Nb, Ta
  - Hetero- 12 – 50 elements possible
  - Lacunary possible
- Can be extremely soluble
- Potential “Designer” material
  - Redox properties
  - High charge
  - High ionic weight
  - High charge delocalization

10 Å
AMT Properties

- Isopolymetalate
- Formula: \((\text{NH}_4)_6[\text{H}_2\text{W}_{12}\text{O}_{40}] \cdot 5\text{H}_2\text{O}\)
- MW = 2958 g/mol (plus ~5 H\(_2\)O)
- Solubility: 2 kg/L
- Charge localization: broad
- Keggin structure with two H heteroatoms
- pH of aqueous solution ~3
Acknowledgements:

U. S. Department of Energy
Valri Lightner
Nancy Garland

Bob Fillnow
Jeff Dann
Frank Venskytis
Tim Bard
Tom Wolfe
Paul Sedor
Héctor Abreuña
Stan Whittingham
Piotr Zelenay
Tommy Rockward
Francisco Uribe
Mike Hickner