Tungsten Cathode Catalyst for PEM Cells

2006 DOE Hydrogen, Fuel Cells Infrastructure
Technologies Program Review

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OSRAM SYLVANIA Products Inc.

May 17, 2006

Project ID# FCP 40

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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/cm^3 @ 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

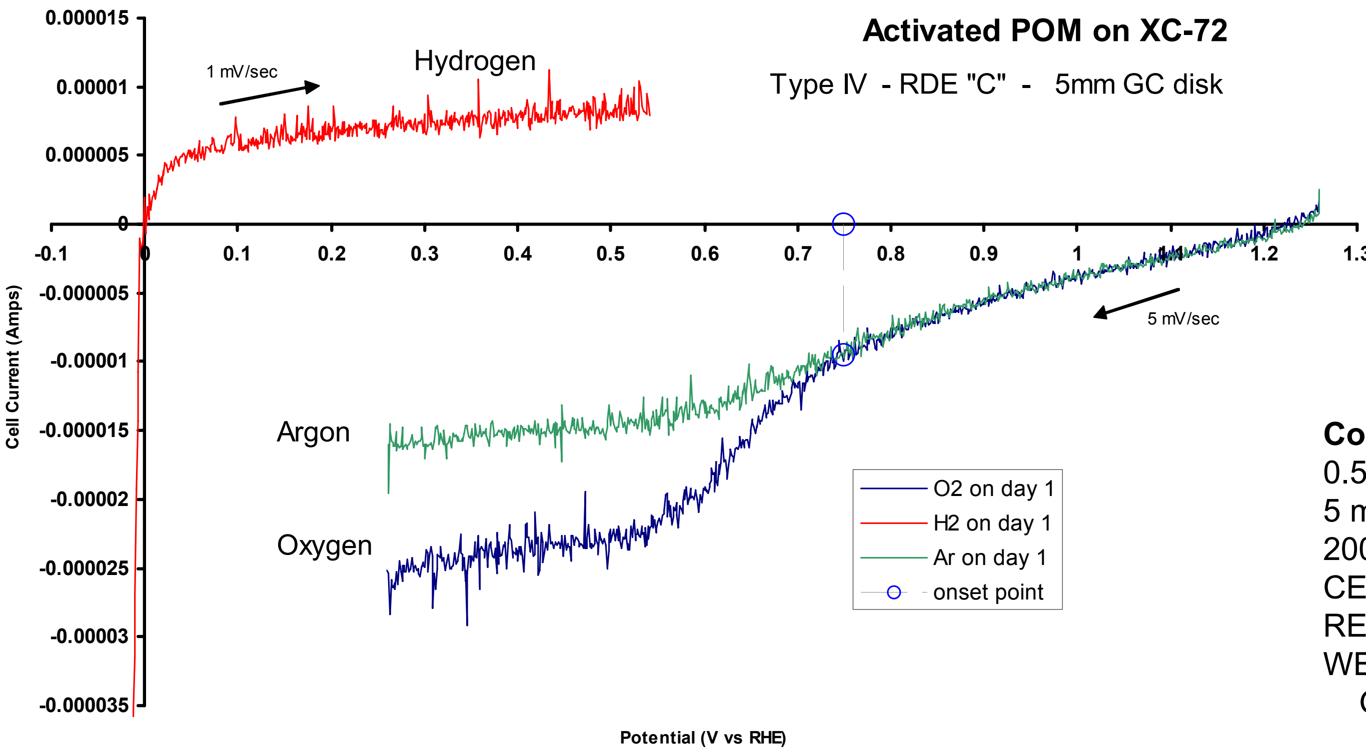
Technical Accomplishments

- 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

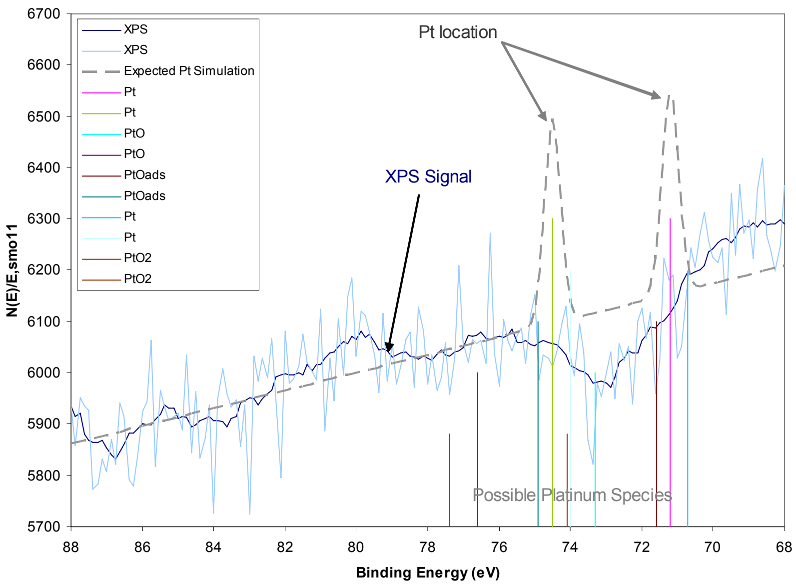
Tungsten Only Cell — RDE (anode and cathode)



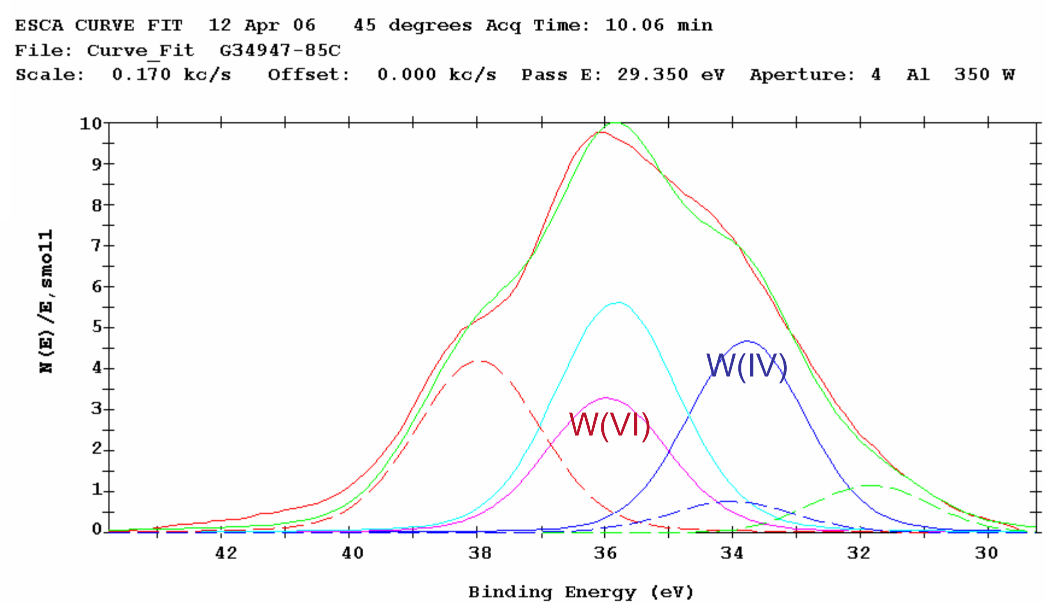
Conditions:
0.5 M HClO4
5 mV/sec
2000 RPM
CE: Carbon Rod
RE: SCE (Hg/Ag)
WE: Thin film on Glassy Carbon

Demonstration of Catalytic Activity

Tungsten Only Cell — RDE

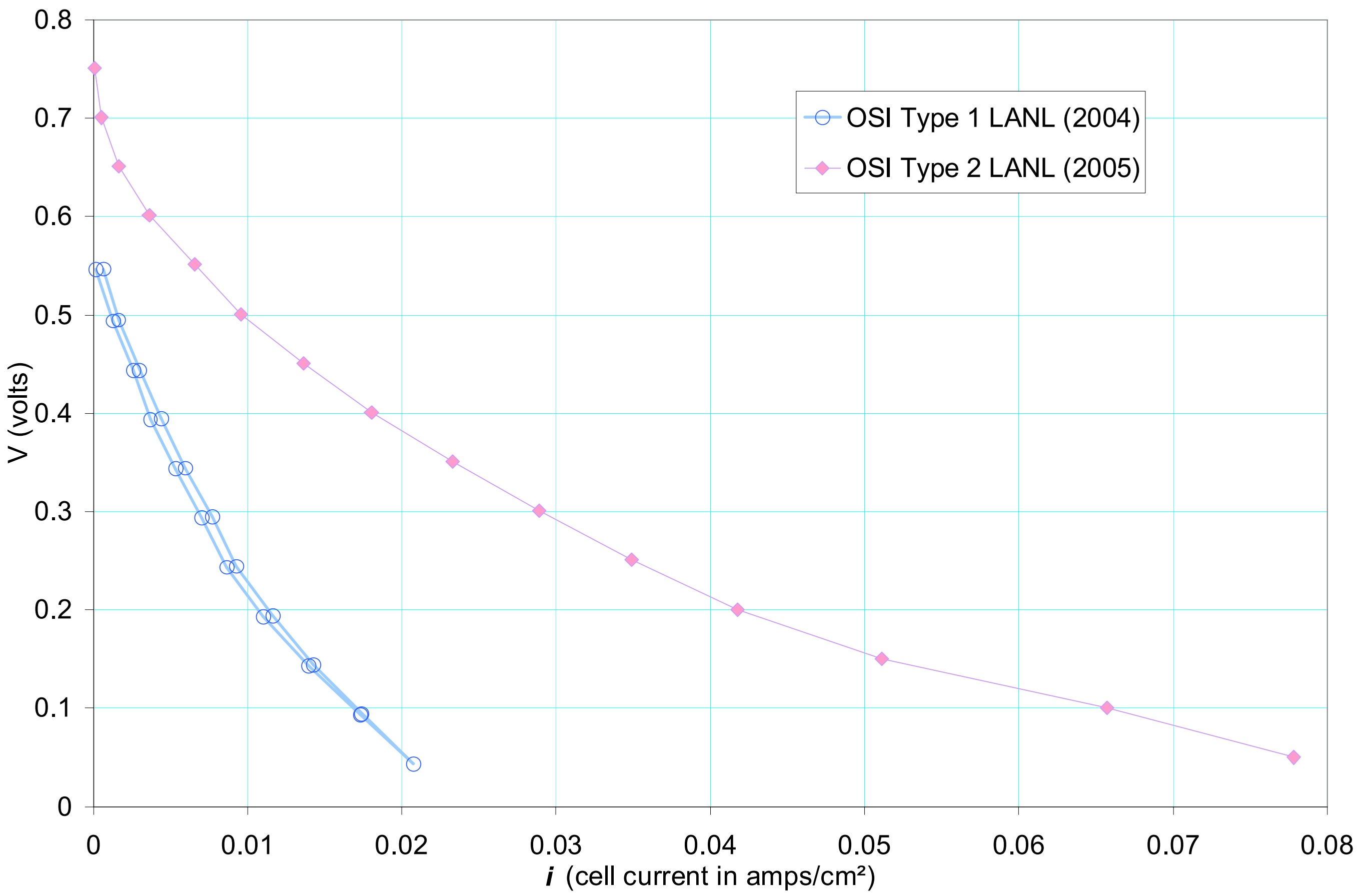


XPS Analysis of RDE Surface



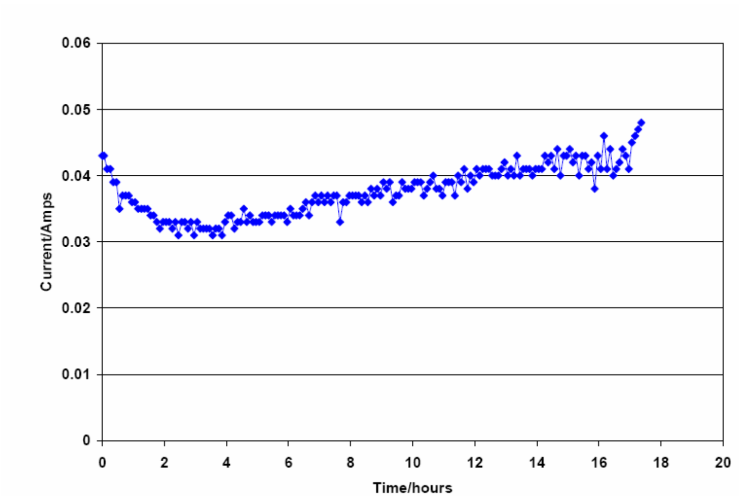
- platinum undetected
- XPS shows reduced W(IV) present

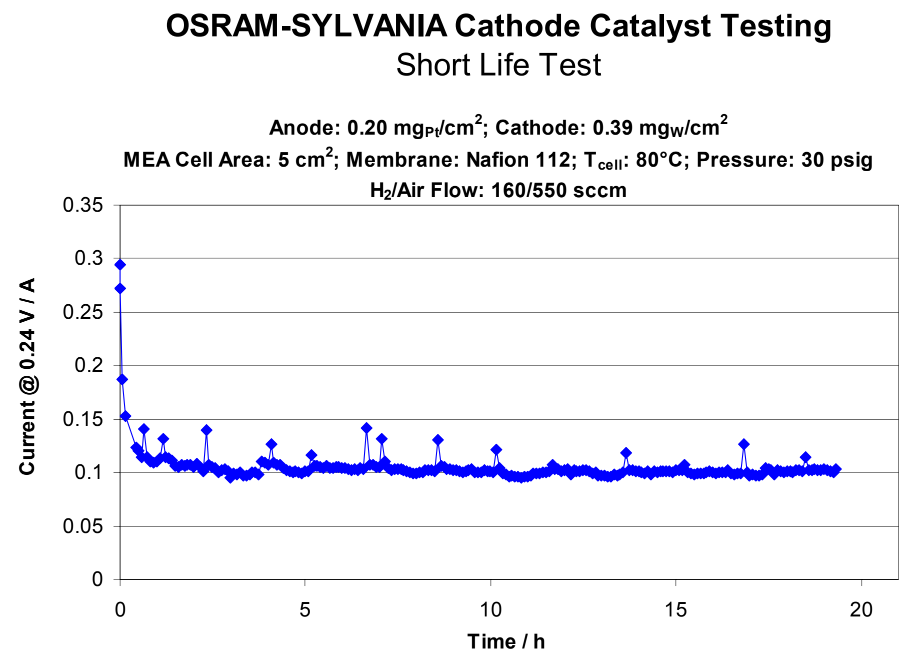
Project Results – LANL Testing



Activity Improved to 0.078 A/cm²

Project Results – LANL Testing



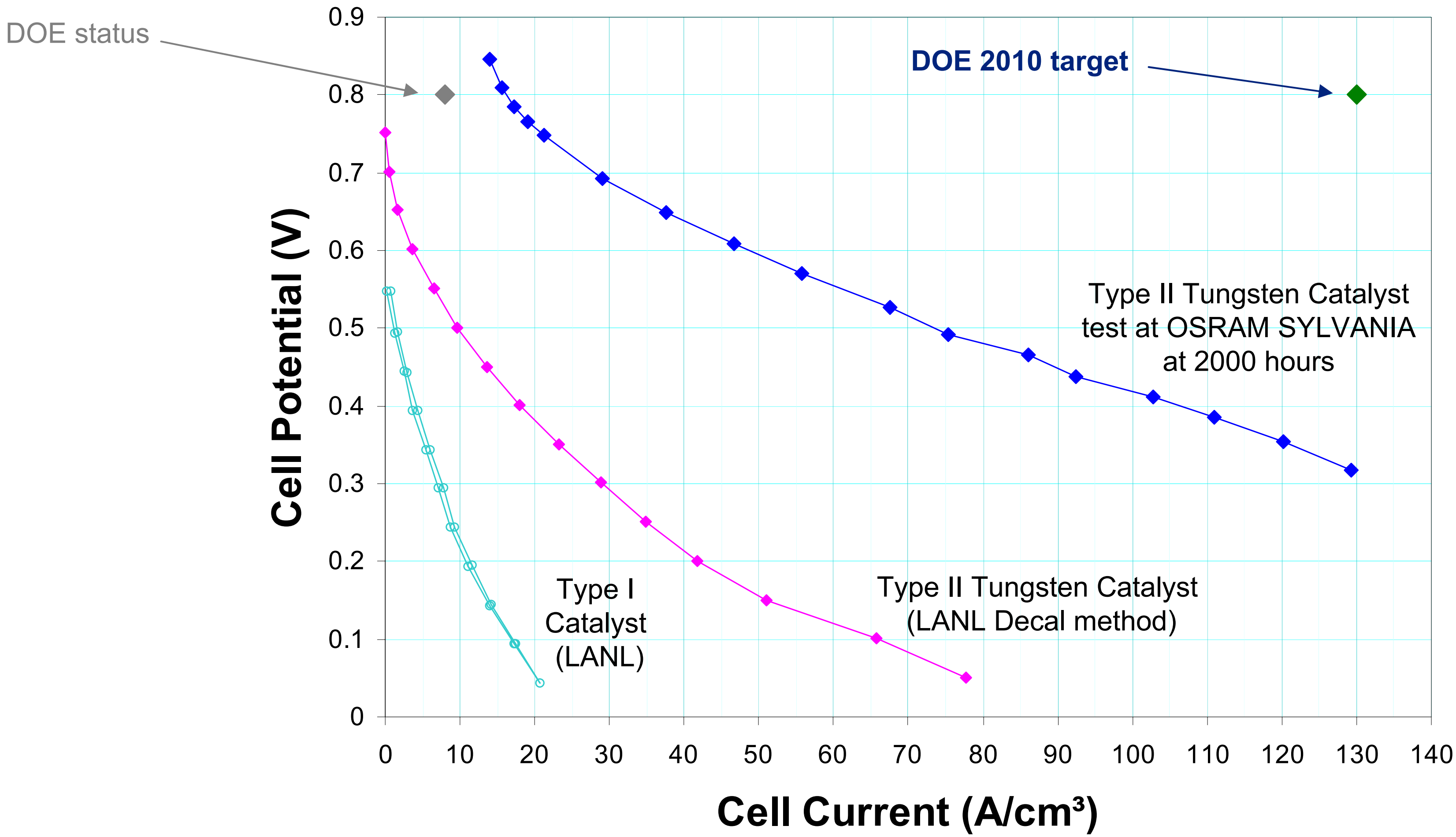


2004 | 2005

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

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

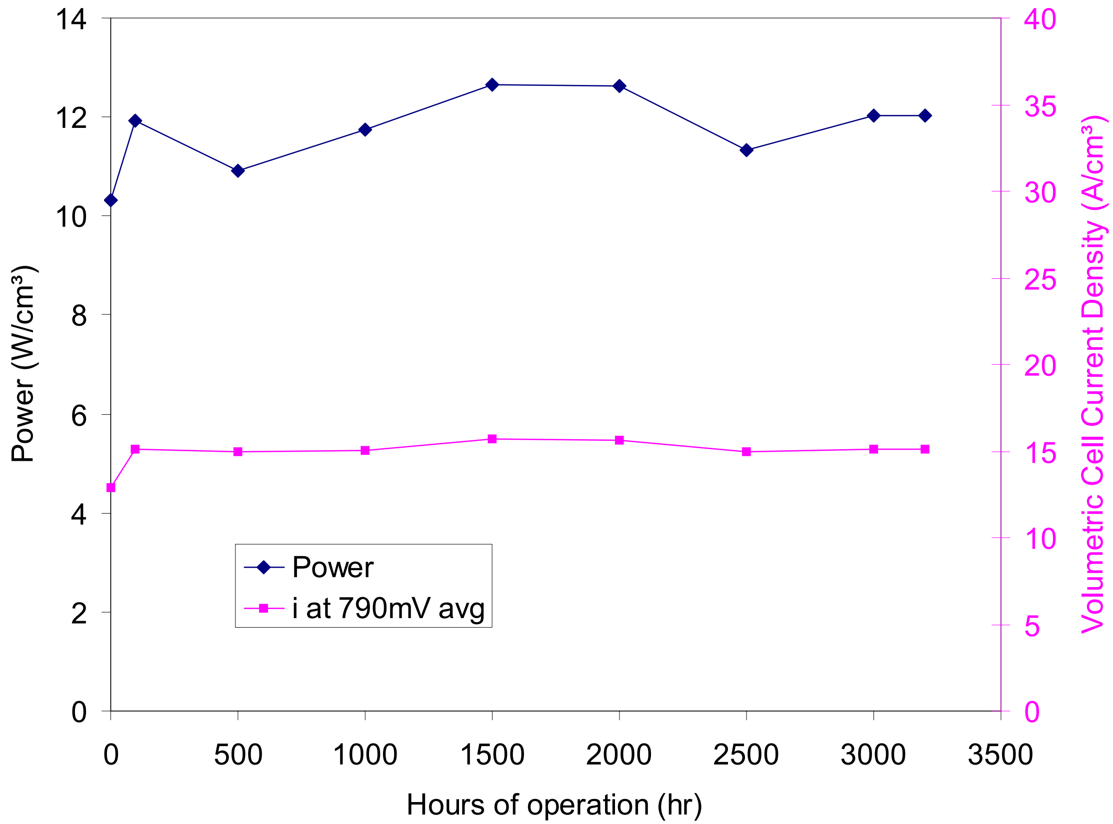
Project Results – Current Output at 2000 hrs



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

60°C, H_2:Air, without iR correction, test at OSRAM SYLVANIA

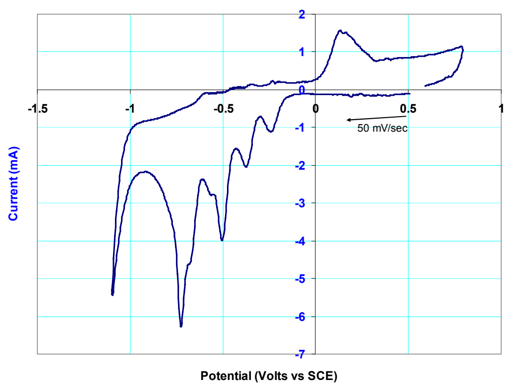
Project Results - Life



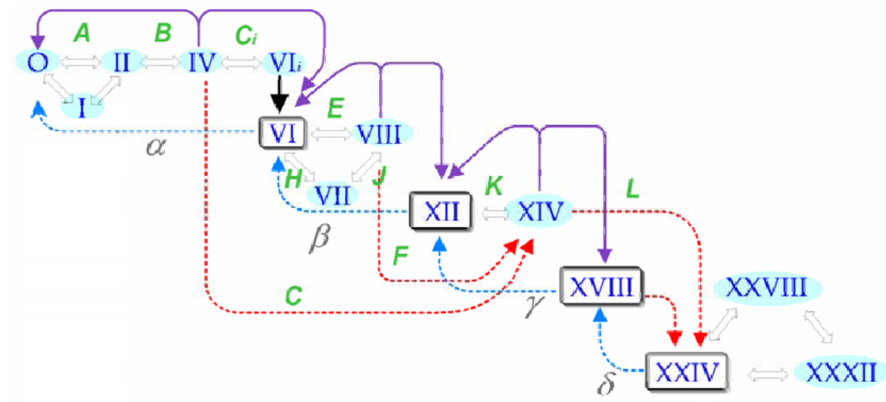
No Degradation in Cell Performance to 3200 Hours

H_2:Air, initially RT then 60°C

Accomplishments – Activation Task

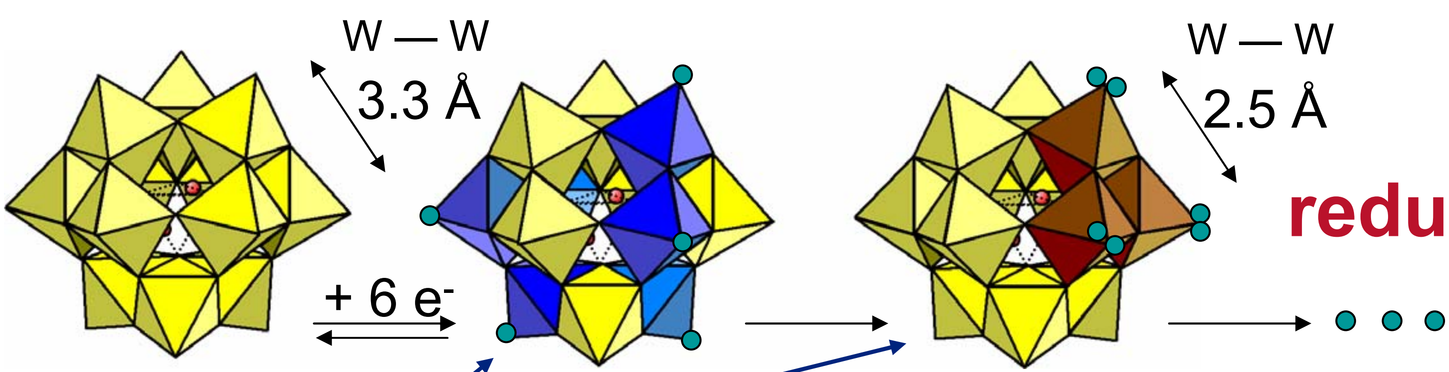


Cyclic Voltammogram of $Na_6[H_2W_{12}O_{40}]$ precursor



Reduction Pathway for Metatungstate

Source: Launay, JINC **38**, 807 (1976)



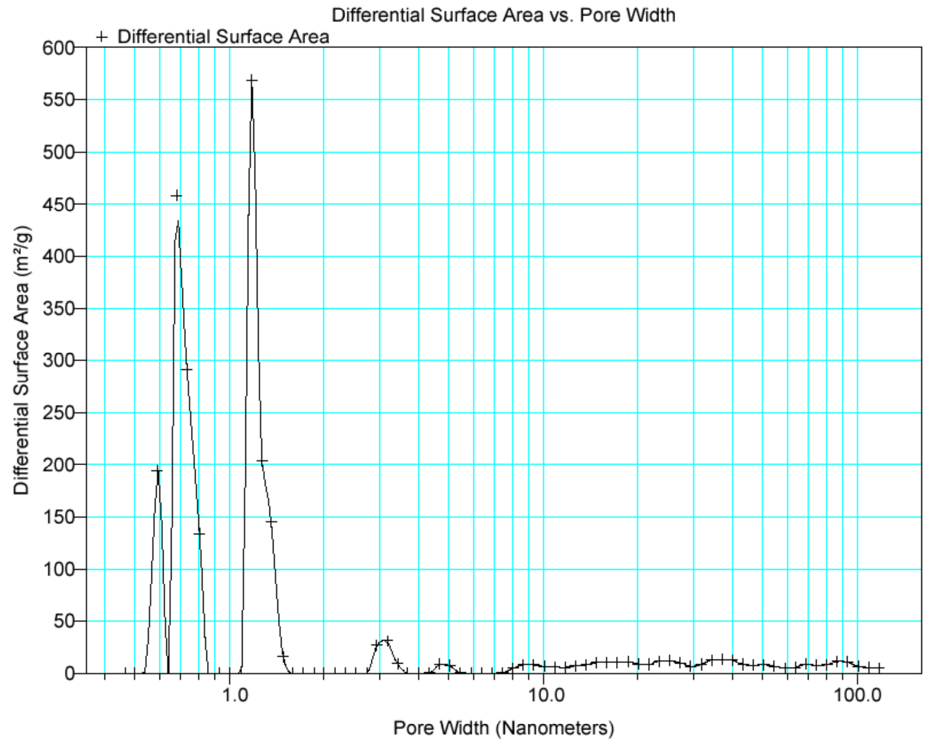
Source: Jeannin, IC 1980 p 2933

re-arrangement changes geometry

Precursor loading on carbon

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

Volume in Pores	<	0.465 nm	:	0.00805 cm³/g
Total Volume in Pores	<=	117.233 nm	:	0.24863 cm³/g
Area in Pores	>	117.233 nm	:	74.186 m²/g
Total Area in Pores	>=	0.465 nm	:	153.665 m²/g

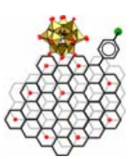


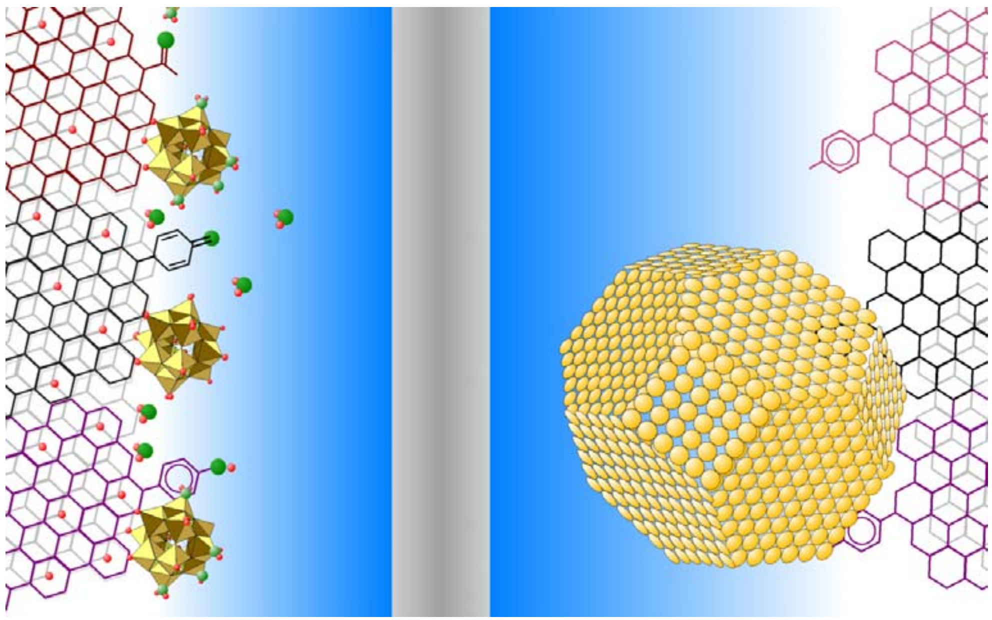
Pore Size Distribution of XC-72

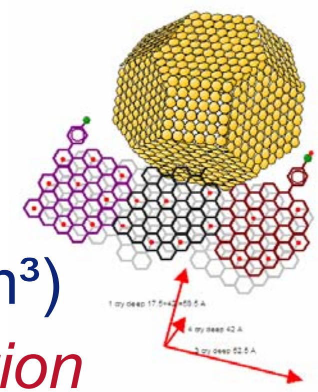
Future Work

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

Idealized polytungstate and Pt electrode surfaces







16 (10^{20}sites/cm³)

75% Metal Utilization

7.6 (10^{20}sites/cm³)

5% Metal Utilization

SYLVANIA

Tungsten catalyst on track to meet the 2010 targets

Mat'l	TOF	SD	SD_{MAX}	A/cm³
Pt[2]	25	3.2	7.6[1,4]	1300
W—POM (current)	1.59	0.62	16[4]	16
2010 POM	**2**	**4.2** *6.77x*		**136**
POM_{MAX}	5	16		1300
req'd[3]	1.6-4	3.1		60 - 160

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

SD = site density
(10^{20} catalytic sites per cm^3)

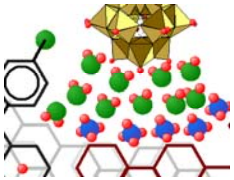
ref 1: Fuel Cell Handbook v2 p 471, citing Kinoshita

ref 2: Gasteiger et al, Appl Cat B 56 (2005) 9-35

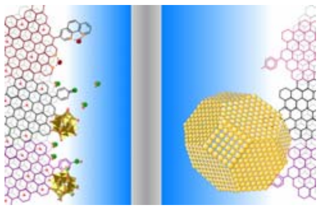
ref 3: Wagner et al, DOE Workshop 3/20/03

ref 4: lecture notes, Jim Benushi, Cabot Corp.

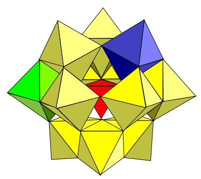
Areas for Improvement



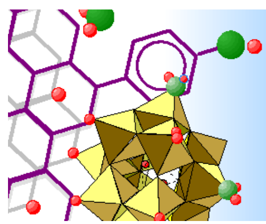
Charge Transfer Kinetics (TOF)



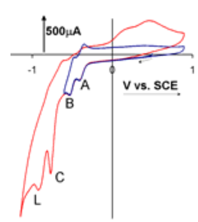
Active Sites (SD)



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/cm^3

Summary

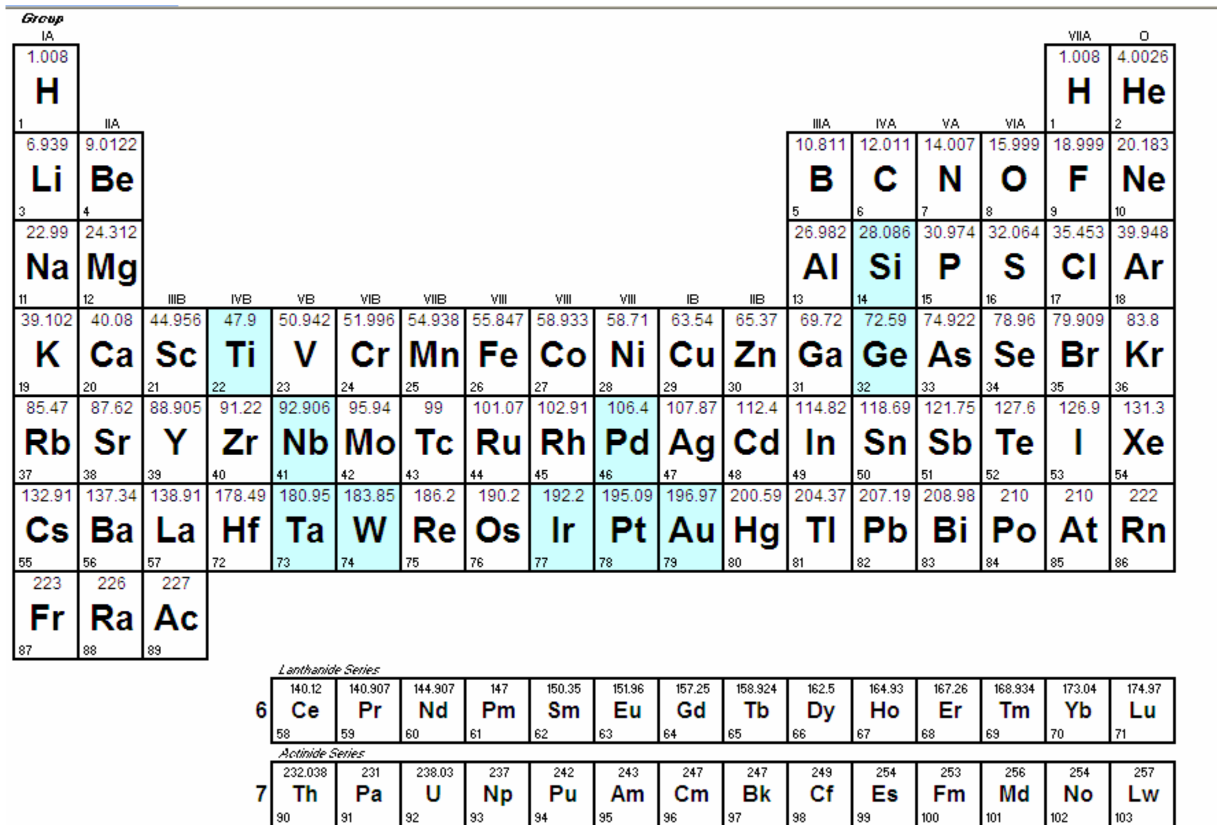
- Catalysis demonstrated on rotated disk electrode
  - anode and cathode catalysis
- PEM Cell performance demonstrated
  - above DOE's non-precious metal 2004 status
  - cathode operation to 3200 hours
  - project milestone exceeded
- Space model shows on-track to 2010 target
  - plan proposed to achieve 130 A/cm^3

Backup Slides

Critical Assumptions and Issues

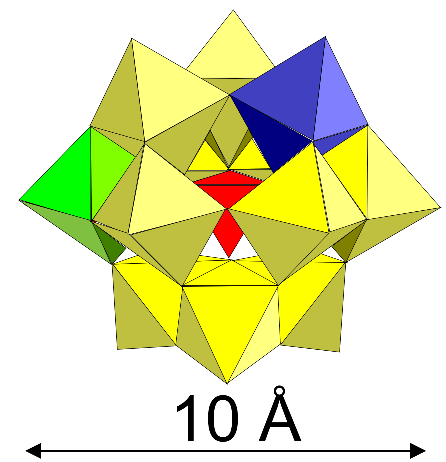
- Adventitious Platinum
  - Pt could migrate across membrane during
    - synthesis/activation
    - operation
  - Protocol is needed to assess effect in PEM cell
    - detection of Pt in non-Pt catalyst area
    - quantification of Pt in non-Pt catalyst area
    - performance effect of Pt in non-Pt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

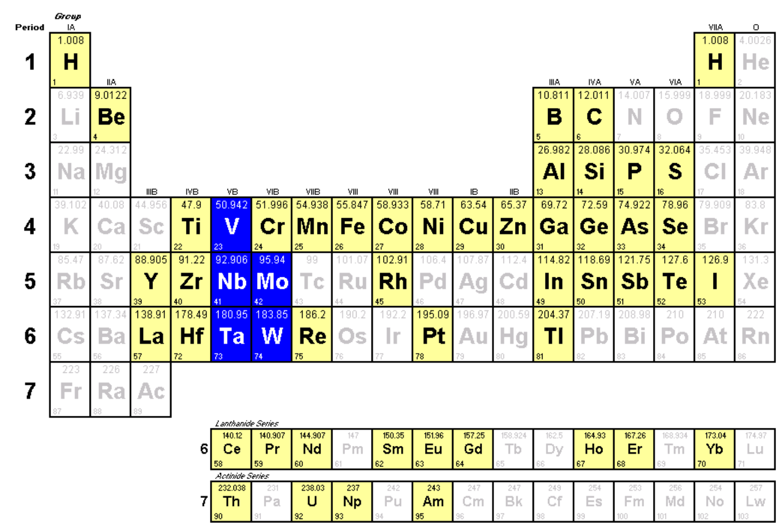
Acid Resistant Elements



Polyoxometalate (POM) - Features

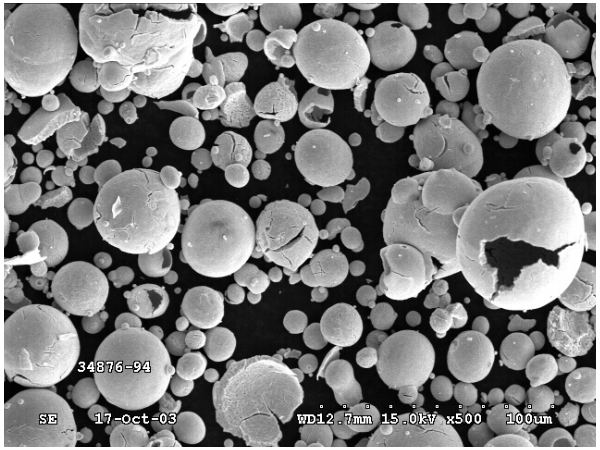
- Keggin type shown
- One central heteroatom
- Octahedra of WO_6 “poly”atoms
- Substituted “poly”atoms
  - Poly- W, Mo, V, Nb, Ta
  - Hetero- 12 – 50 elements possible
  - Lacunary possible
- Can be extremely soluble
- Potential “Designer” material
  - Redox properties
  - High charge
  - High ionic weight
  - High charge delocalization

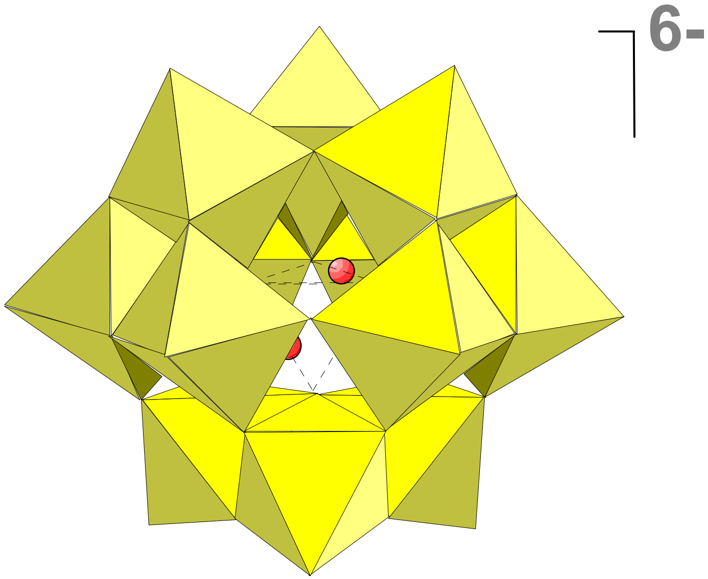




AMT Properties

- Isopolymetalate
- Formula: $\mathbf{(NH_4)_6[H_2W_{12}O_{40}] \cdot 5H_2O}$
- MW = 2958 g/mol (plus ~5 H_2O)
- 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 Abruña
Stan Whittingham
Piotr Zelenay
Tommy Rockward
Francisco Uribe
Mike Hickner