

Tungsten Cathode Catalyst for PEM Cells

2006 DOE Hydrogen, Fuel Cells Infrastructure
Technologies Program Review

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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

- $> 130 \text{ A/cm}^3 @ 0.8\text{V}$

Durability

- 5000 hours (cycling)

Cost

- $< 8 \text{ \$/kW}$

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

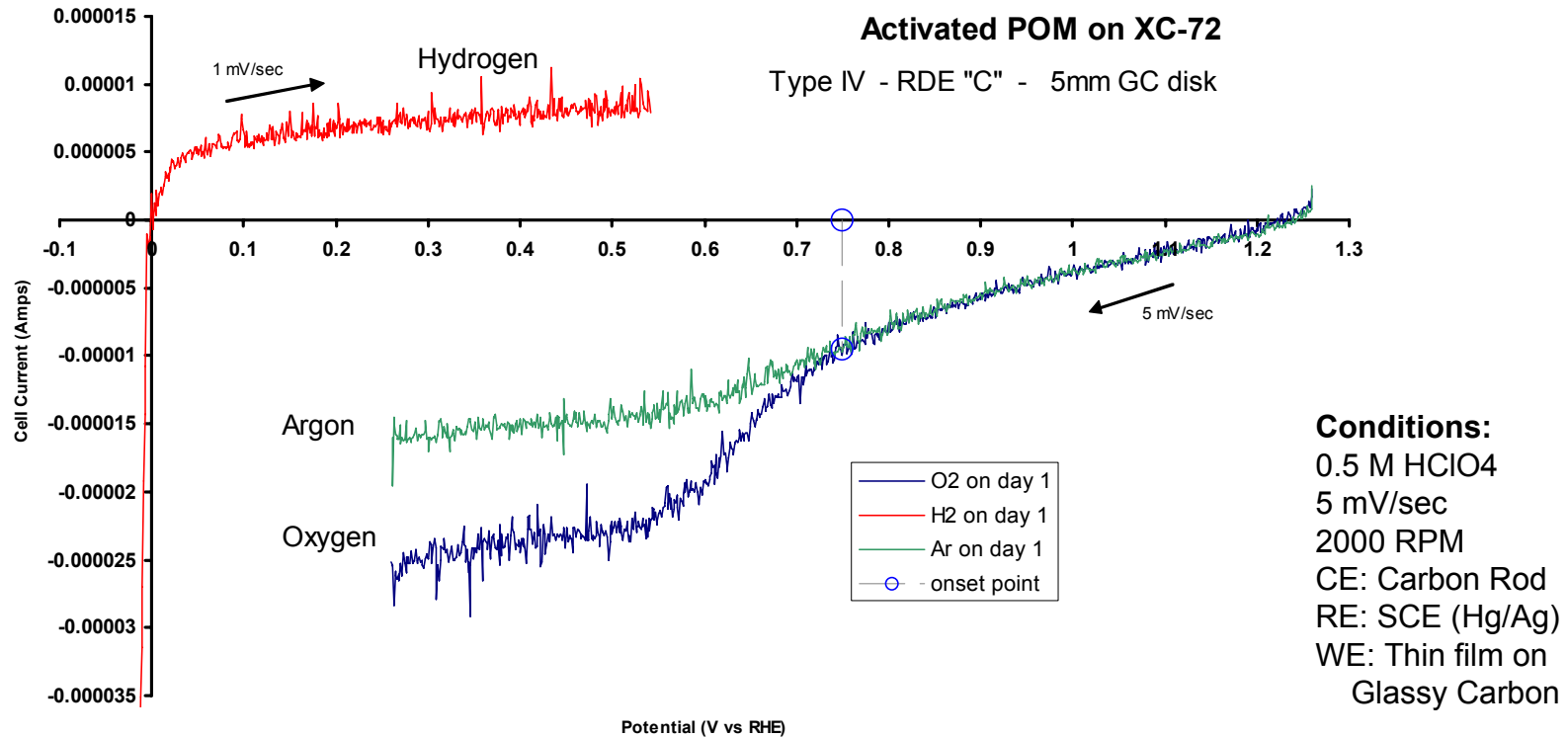
Technical Accomplishments

- 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

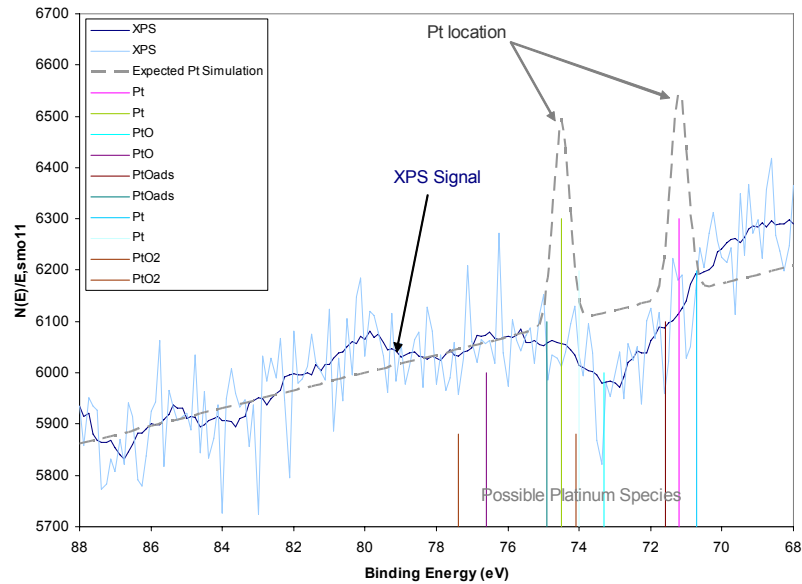
- Completed work in 5 key tasks:
 - activation conditions
 - precursor composition
 - precursor loading on carbon
 - ink formulation
 - analysis
- Composition change provided the increase in cathode performance

Tungsten Only Cell — RDE (anode and cathode)



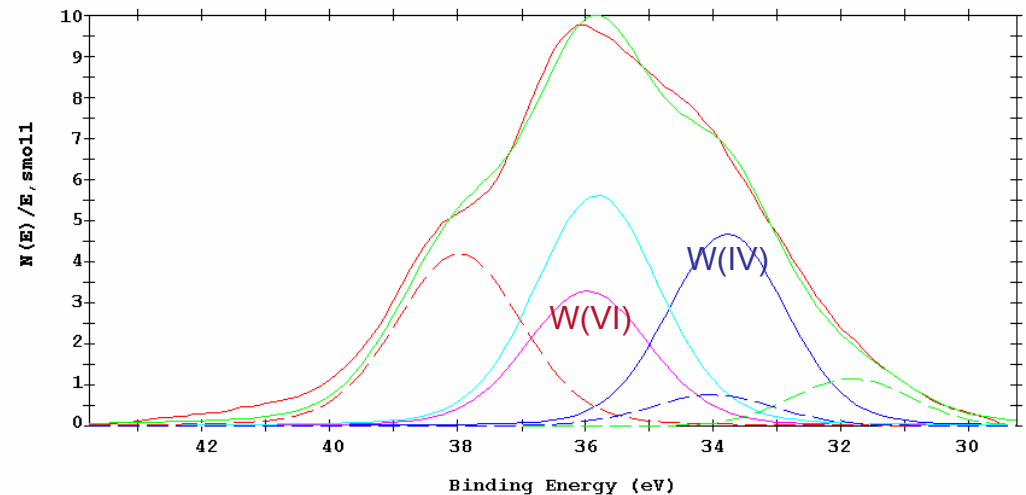
Demonstration of Catalytic Activity

Tungsten Only Cell — RDE



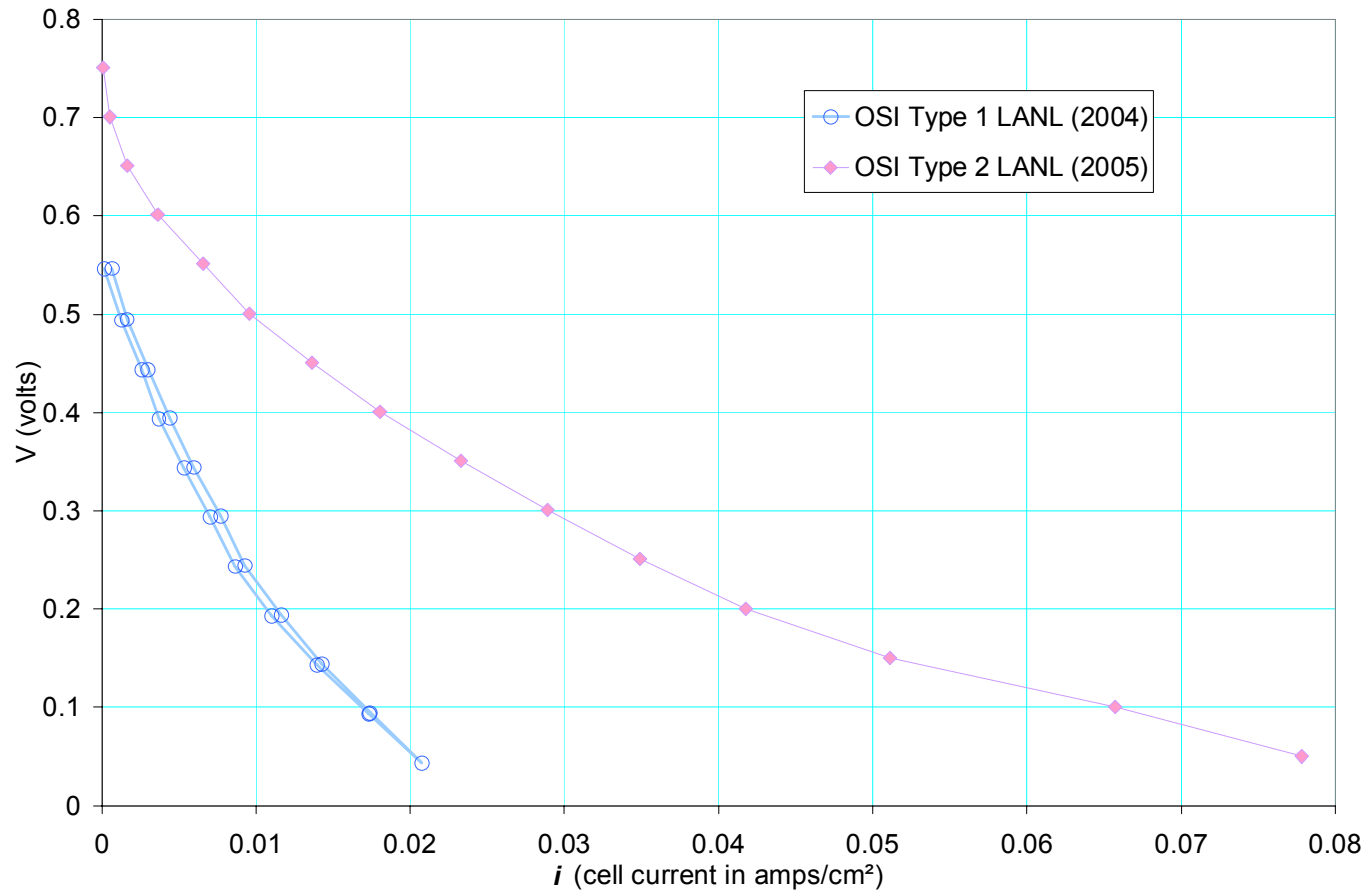
XPS Analysis of RDE Surface

ESCA CURVE FIT 12 Apr 06 45 degrees Acq Time: 10.06 min
File: Curve_Fit_G34947-85C
Scale: 0.170 kc/s Offset: 0.000 kc/s Pass E: 29.350 eV Aperture: 4 Al 350 W



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

Project Results – LANL Testing

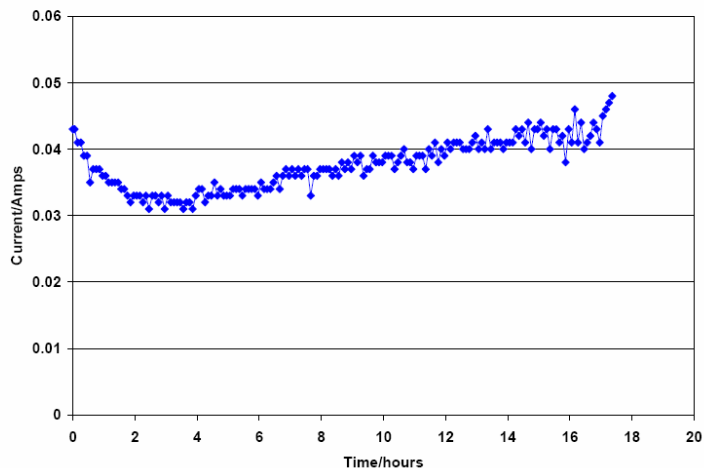


Activity Improved to 0.078 A/cm²

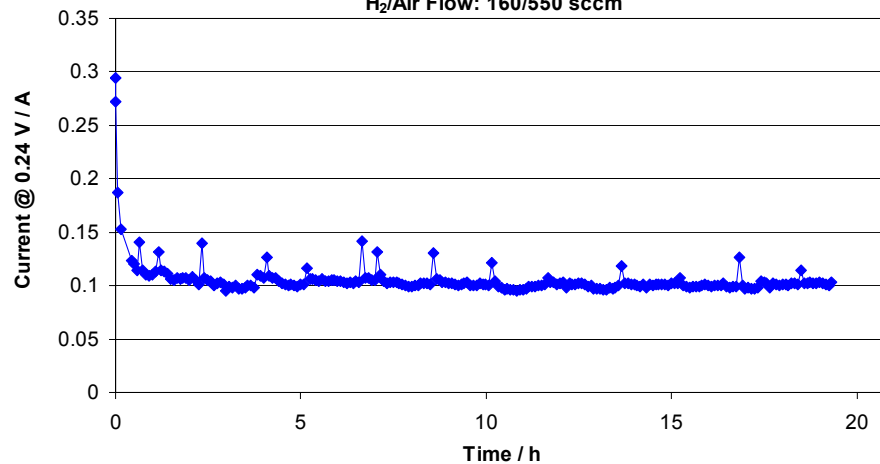
Project Results – LANL Testing

OSRAM-SYLVANIA Cathode Catalyst Testing Short Life Test

Anode: $0.20 \text{ mg}_{\text{Pt}}/\text{cm}^2$; Cathode: $0.39 \text{ mg}_{\text{W}}/\text{cm}^2$
MEA Cell Area: 5 cm^2 ; Membrane: Nafion 112; T_{cell} : 80°C ; Pressure: 30 psig
 H_2/Air Flow: 160/550 sccm



2004



2005

20 hour life test at 0.24V shows 2.5x improvement to $0.02 \text{ A}/\text{cm}^2$

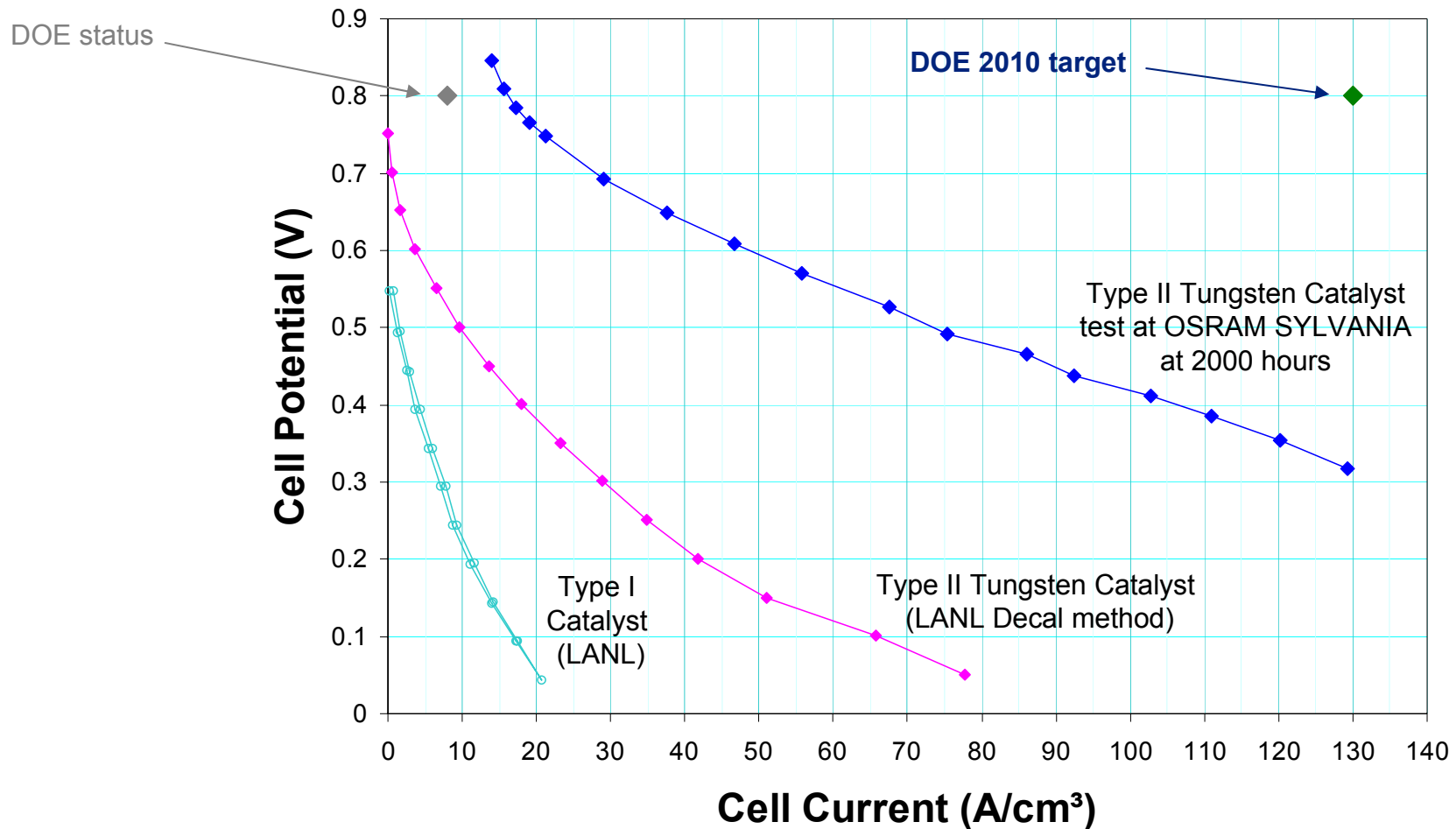
both tests at 0.24V, 5cm^2 cell

2004 Test: $\sim 0.04 \text{ A}$ in cell = $0.008 \text{ A}/\text{cm}^2$

2005 Test: 0.1 A in cell = $0.02 \text{ A}/\text{cm}^2$

This comparison shows an improvement of 2.5x, project milestone was 2x

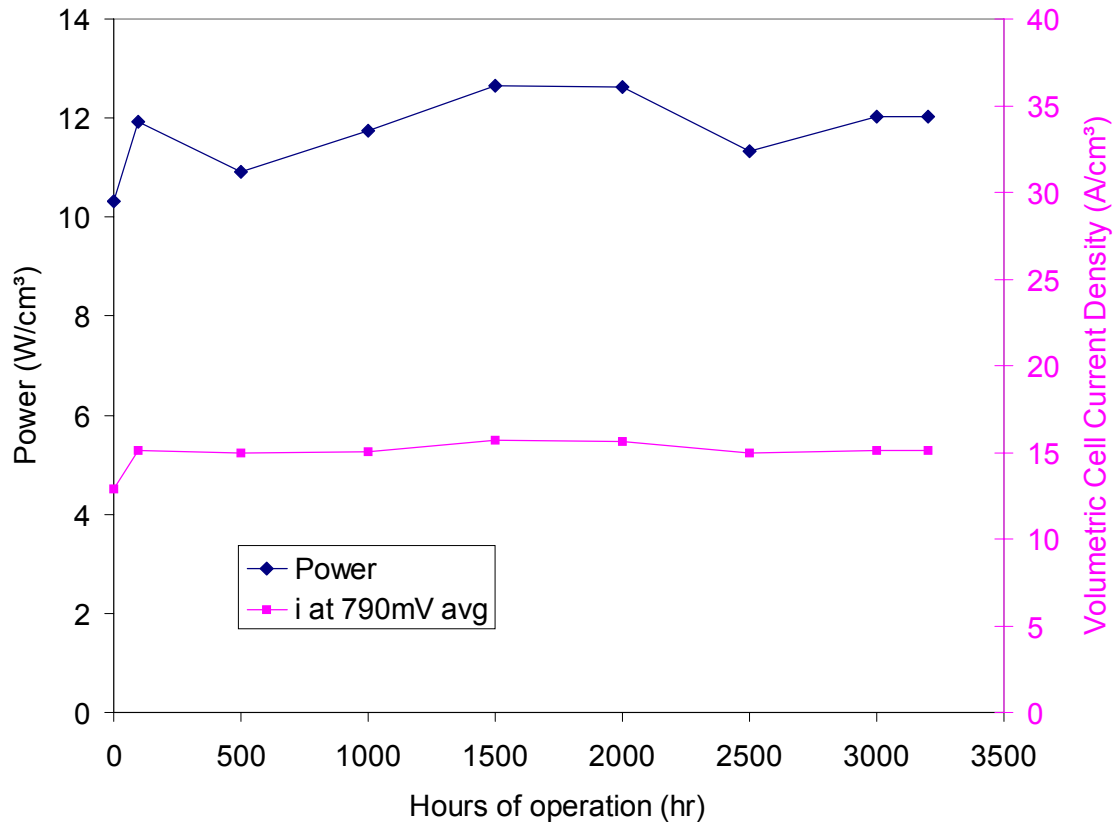
Project Results – Current Output at 2000 hrs



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

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

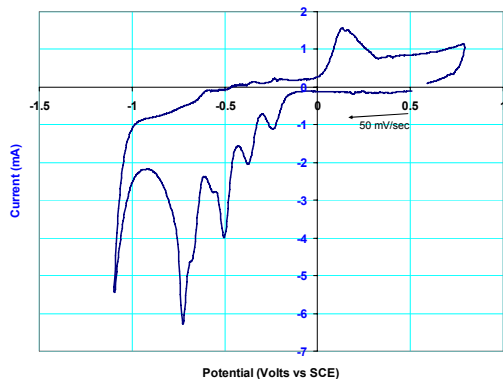
Project Results - Life



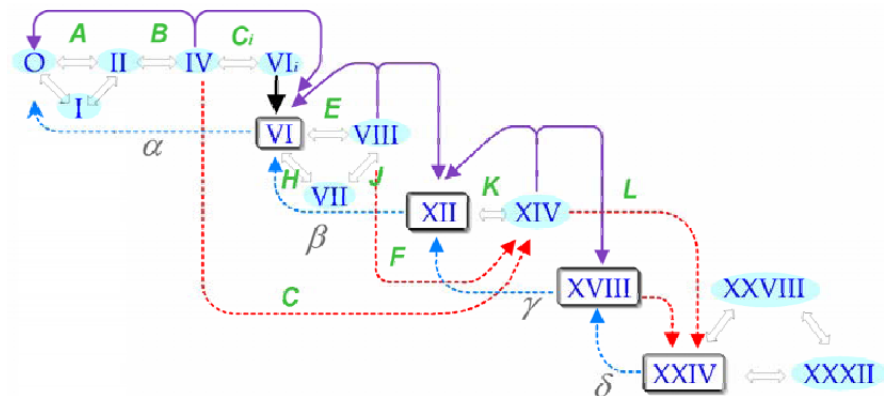
No Degradation in Cell Performance to 3200 Hours

H_2 :Air, initially RT then 60°C

Accomplishments – Activation Task

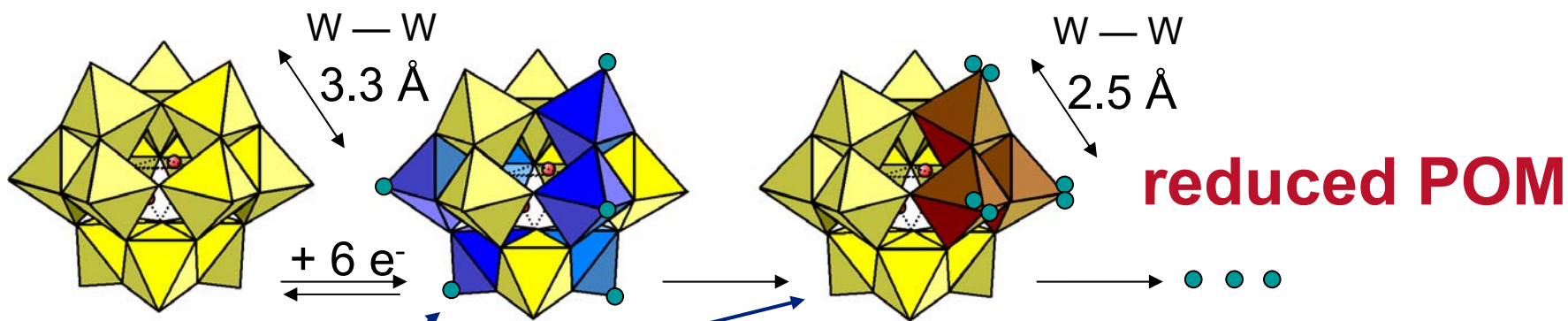


Cyclic Voltammogram of $\text{Na}_6[\text{H}_2\text{W}_{12}\text{O}_{40}]$ precursor



Reduction Pathway for Metatungstate

Source: Launay, JINC 38, 807 (1976)



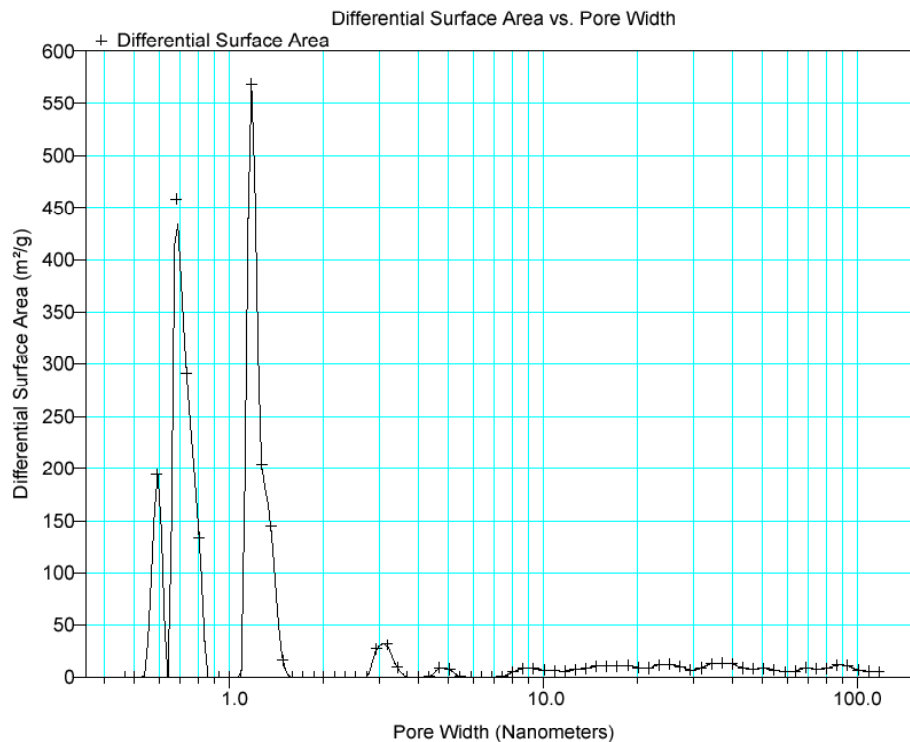
Source: Jeannin, IC 1980 p 2933

re-arrangement changes geometry

Precursor loading on carbon

Volume in Pores	<	0.465 nm	:	0.00805 cm ³ /g
Total Volume in Pores	<=	117.233 nm	:	0.24863 cm ³ /g
Area in Pores	>	117.233 nm	:	74.186 m ² /g
Total Area in Pores	>=	0.465 nm	:	153.665 m ² /g

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

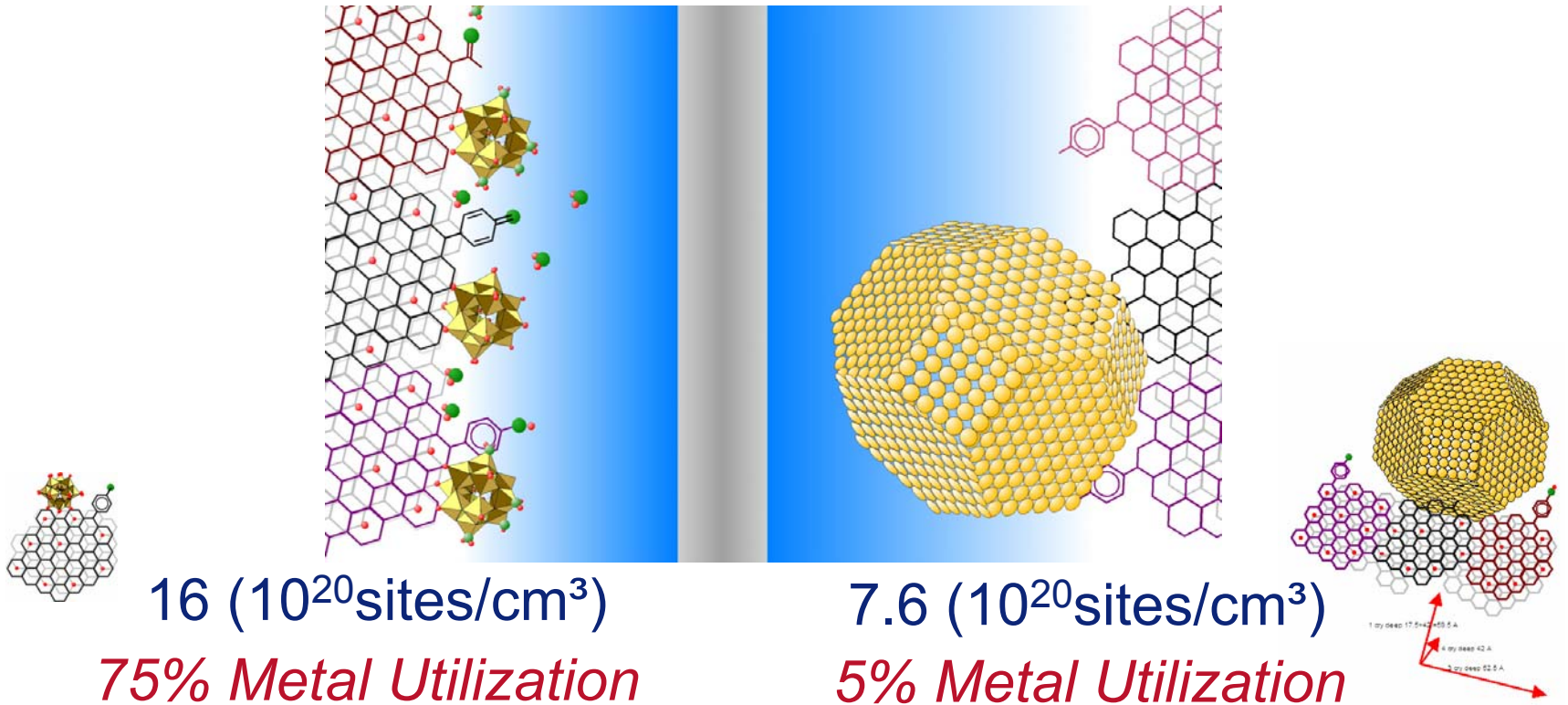


Pore Size Distribution of XC-72

Future Work

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

Idealized polytungstate and Pt electrode surfaces



Tungsten catalyst on track to meet the 2010 targets

Mat'l	TOF	SD	SD _{MAX}	A/cm ³
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
(10²⁰ catalytic sites per cm³)

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

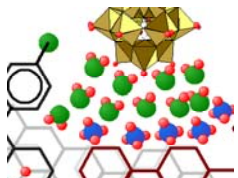
ref 2: Gasteiger et al, Appl Cat B 56 (2005) 9-35

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

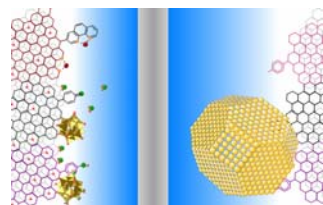
ref 4: lecture notes, Jim Benushi, Cabot Corp.



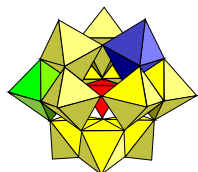
Areas for Improvement



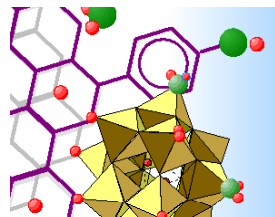
Charge Transfer Kinetics (TOF)



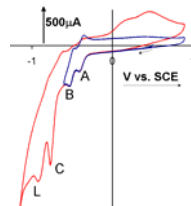
Active Sites (SD)



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

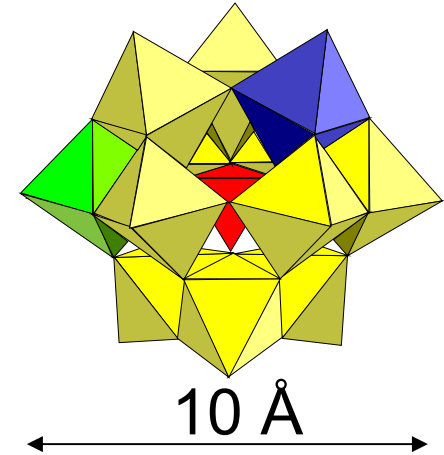
- Adventitious Platinum
 - Pt could migrate across membrane during
 - synthesis/activation
 - operation
 - Protocol is needed to assess effect in PEM cell
 - detection of Pt in non-Pt catalyst area
 - quantification of Pt in non-Pt catalyst area
 - performance effect of Pt in non-Pt catalyst area
 -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

Acid Resistant Elements

Group											VIA				O		
1.008 H											1.008 H	4.0026 He					
6.939 Li	9.0122 Be											10.811 B	12.011 C	14.007 N	15.999 O	18.999 F	20.183 Ne
22.99 Na	24.312 Mg											26.982 Al	28.086 Si	30.974 P	32.064 S	35.453 Cl	39.948 Ar
39.102 K	40.08 Ca	44.956 Sc	47.9 Ti	50.942 V	51.996 Cr	54.938 Mn	55.847 Fe	58.933 Co	58.71 Ni	63.54 Cu	65.37 Zn	69.72 Ga	72.59 Ge	74.922 As	78.96 Se	79.909 Br	83.8 Kr
85.47 Rb	87.62 Sr	88.905 Y	91.22 Zr	92.906 Nb	95.94 Mo	99 Tc	101.07 Ru	102.91 Rh	106.4 Pd	107.87 Ag	112.4 Cd	114.82 In	118.69 Sn	121.75 Sb	127.6 Te	126.9 I	131.3 Xe
132.91 Cs	137.34 Ba	138.91 La	178.49 Hf	180.95 Ta	183.85 W	186.2 Re	190.2 Os	192.2 Ir	195.09 Pt	196.97 Au	200.59 Hg	204.37 Tl	207.19 Pb	208.98 Bi	210 Po	210 At	222 Rn
223 Fr	226 Ra	227 Ac															
<i>Lanthanide Series</i>																	
6	140.12 Ce	140.907 Pr	144.907 Nd	147 Pm	150.35 Sm	151.96 Eu	157.25 Gd	158.924 Tb	162.5 Dy	164.93 Ho	167.26 Er	168.934 Tm	173.04 Yb	174.97 Lu			
<i>Actinide Series</i>																	
7	232.038 Th	231 Pa	238.03 U	237 Np	242 Pu	243 Am	247 Cm	247 Bk	249 Cf	254 Es	253 Fm	256 Md	254 No	257 Lw			

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



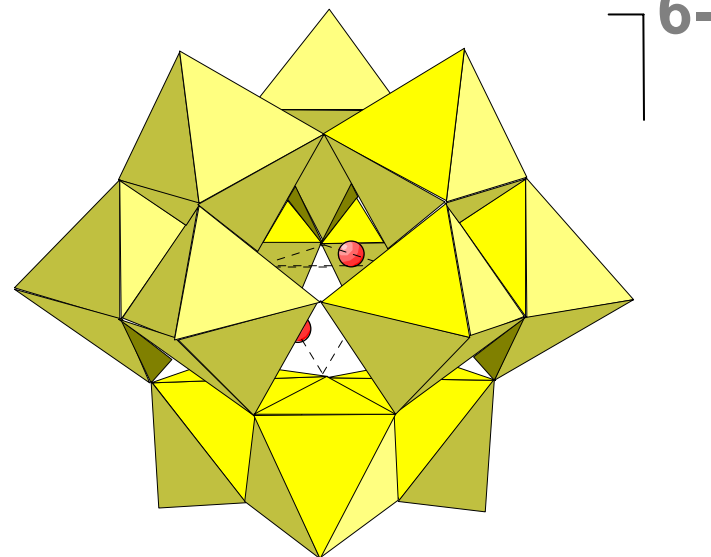
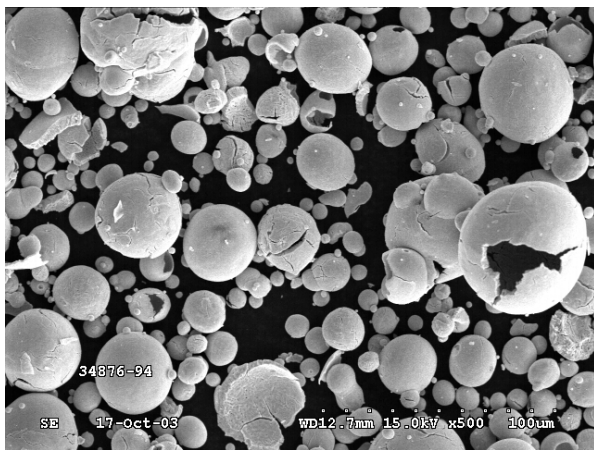
Period	Group IA											VIA	VIIA	VIIIA	IXA	X		
1	H 1.008											H 1.008	He 4.0026					
2	Li 6.941	Be 9.0122											B 10.811	C 12.011	N 14.007	O 15.999	F 18.998	Ne 20.183
3	Na 22.99	Mg 24.312											Al 26.982	Si 28.086	P 30.974	S 32.064	Cl 35.453	Ar 39.948
4	K 39.102	Ca 40.08	Sc 44.956	Ti 47.9	V 50.942	Cr 51.996	Mn 54.938	Fe 55.847	Co 58.933	Ni 58.71	Cu 63.54	Zn 65.37	Ga 69.72	Ge 72.59	As 74.922	Se 78.96	Br 79.904	Kr 83.8
5	Rb 85.47	Sr 87.62	Y 88.905	Zr 91.22	Nb 92.906	Mo 95.94	Tc 99	Ru 101.07	Rh 102.91	Pd 106.4	Ag 107.87	Cd 112.4	In 114.82	Sn 118.69	Sb 121.75	Te 127.6	I 126.9	Xe 131.3
6	Cs 132.9	Ba 137.34	La 138.91	Hf 178.49	Ta 180.95	W 183.85	Re 186.2	Os 190.2	Ir 192.22	Pt 195.09	Au 196.97	Hg 200.59	Tl 204.37	Pb 207.2	Bi 208.98	Po 209	At 210	Rn 222
7	Fr 223	Ra 226	Ac 227															

Lanthanide Series														
6	Ce 140.12	Pr 140.907	Nd 144.24	Pm 144.9126	Sm 150.36	Eu 151.964	Gd 157.25	Tb 158.925	Dy 162.5	Ho 164.93	Er 167.26	Tm 168.934	Yb 173.04	Lu 174.967

Actinide Series														
7	Th 232.038	Pa 231.036	U 238.0289	Np 237	Pu 244	Am 243	Cm 247	Bk 247	Cf 251	Es 252	Fm 257	Md 258	No 259	Lw 261

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 H₂O)
- Solubility: 2 kg/L
- Charge localization: broad
- Keggin structure with two H heteroatoms
- pH of aqueous solution ~3



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