Nanoscale Tantalum Oxide Based Catalysts for PEM Fuel Cell Applications

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Sponsor: PNNL Lab-Fellow LDRD Project

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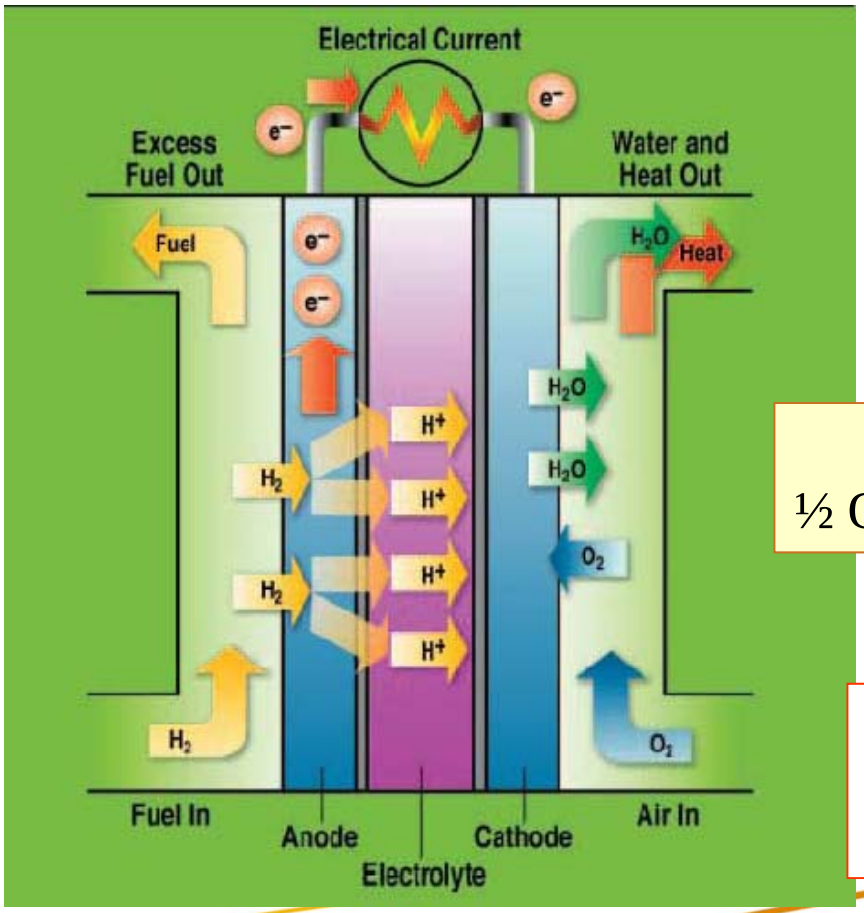
Outline

- Background
  - Critical issues in PEM fuel cells
  - Nanoscale Ta Oxide/Carbon Composite
- Results
  - Effect of W addition on Electrochemical Performance
  - XPS results
- Summary

Proton Exchange Membrane Fuel Cells (PEMFCs)



Anode:

$H_2 \rightarrow 2H^+ + 2\ e^-$

Cathode:

$\frac{1}{2}\ O_2 + 2H^+ + 2\ e^- \rightarrow H_2O$

RDS: Oxygen Reduction Reaction (ORR)

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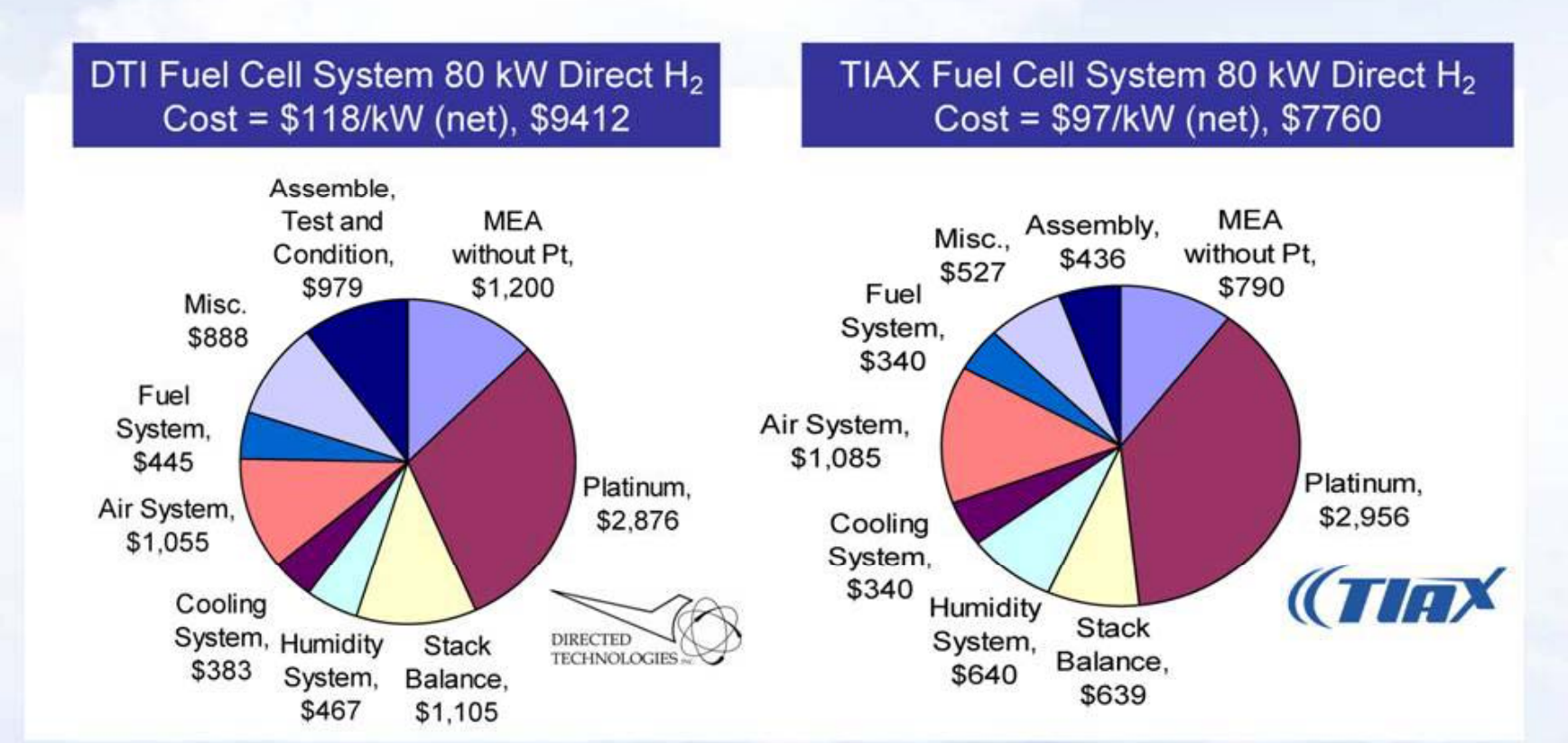
Recent Cost Analyses



2007 DOE (EERE) Hydrogen Program Review

~30% of the cost of a FC system is directly attributable to the Pt catalysts!

Development of non-Pt based catalysts is critical for the commercialization.

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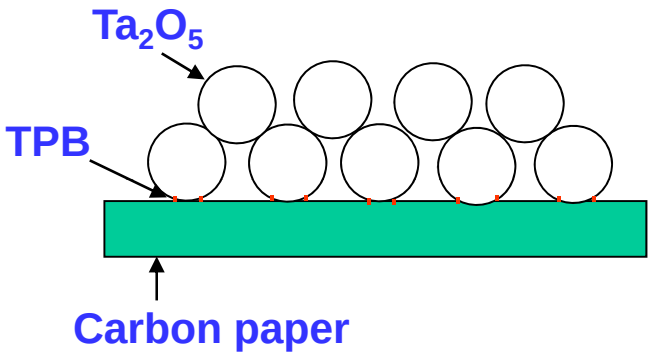
Why Ta Oxide?

- Summary of Previous Results
  - High oxygen reduction potential comparable to Pt
  - Stable under corrosive environments
  - But, Reduction current was limited due to poor electrical conductivity (limited reaction sites, TPB′s)
  - Sputtering of nanoscale Ta oxide was used for feasibility tests to increase the TPB density.
  - The sputtered nanoscale Ta Oxide displayed ~ 1/3 of the mass specific current density of Pt at 60°C and 80°C, even though the area specific current density was limited due to the 2-D structure.

Nanoscale Ta Oxide/Carbon Composite

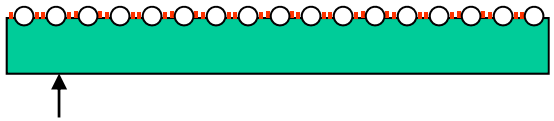
Ta-oxide powder

Low mass spec. current
Low area spec. current

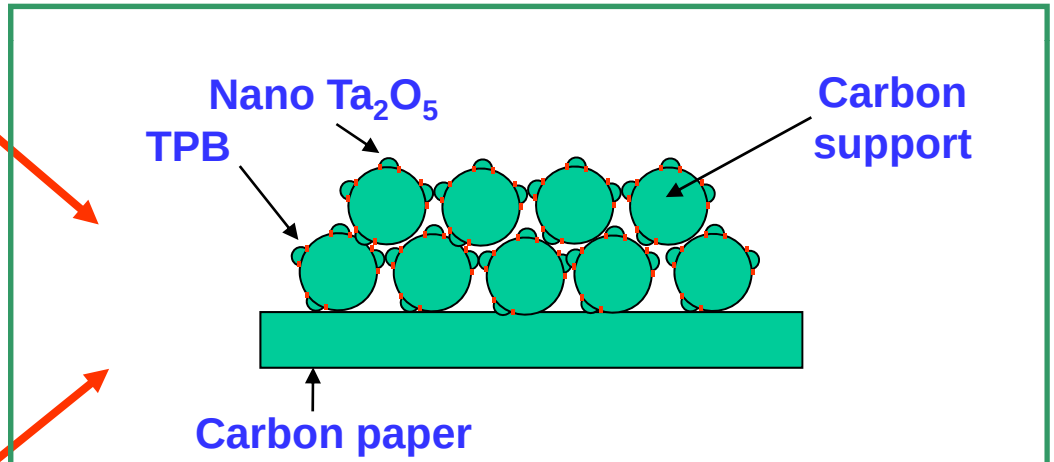


Sputtered Ta-oxide nano particles

High mass spec. current
Low area spec. current



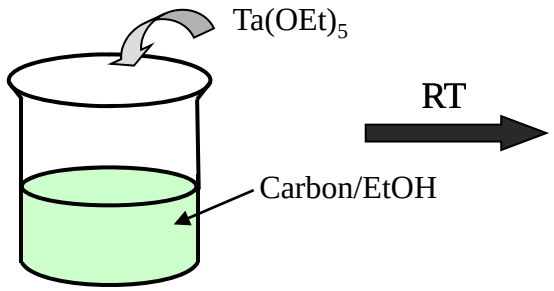
The vehicle to testing our hypothesis



Carbon supported Ta_2O_5 nanoparticles?

High mass spec. current
High area spec. current

Material Synthesis: *Direct Synthesis*

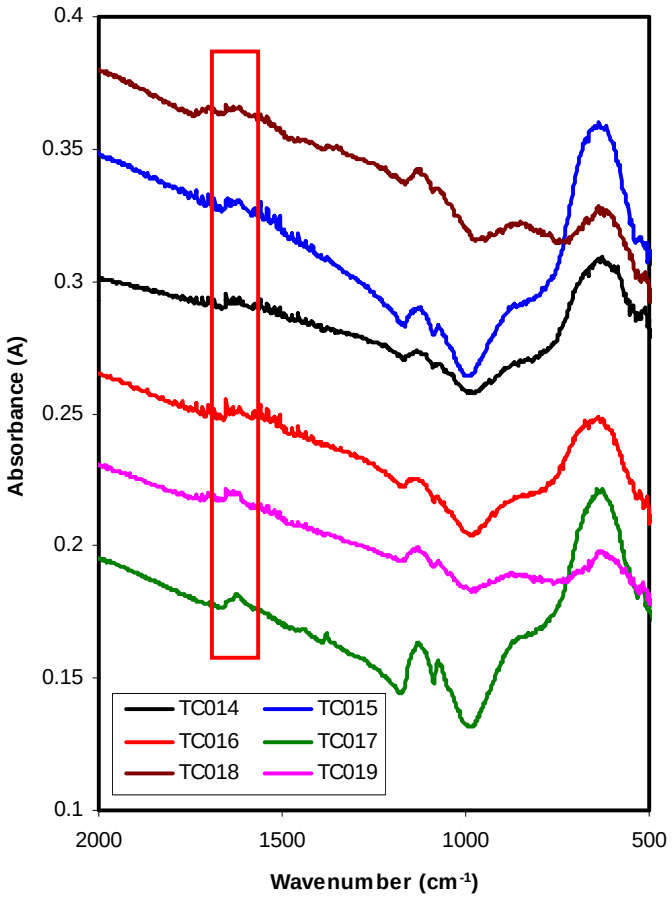


RT

1. **Dried at 60°C under vacuum**
2. **Ball-milling for 15 min**

- No precursor modification and surfactant needed
- Ta_2O_5 particles nucleate on functionalized carbon surface and are distributed homogeneously.
- The covalent bonds b/w Ta_2O_5 and carbon are formed *in-situ* during the process.

FTIR Analysis



Sample ID	carbon	Ta205 /Carbon	Wt% (Ta2O5)	Carbonyl vibration (cm^{-1})
TC014	**A5348R**	1.71	63	1635
TC015	**A5348R**	3.42	77	1635
TC016	**F1-A5348R**	1.71	63	1624
TC017	**F1-A5348R**	3.42	77	1630
TC018	**F2-A5348R**	1.71	63	1633
TC019	**F2-A5348R**	3.42	77	1633

- Direct synthetic process showed strong Ta-O stretching vibration peaks at 520-780 cm^{-1}
- The carbonyl bonds around 1630 cm^{-1} indicate covalent bonds of Ta_2O_5 on the carbon surface

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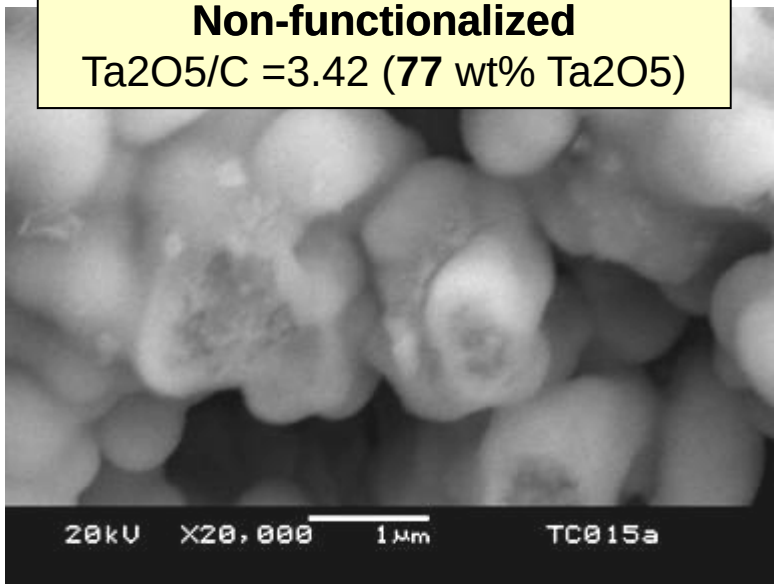
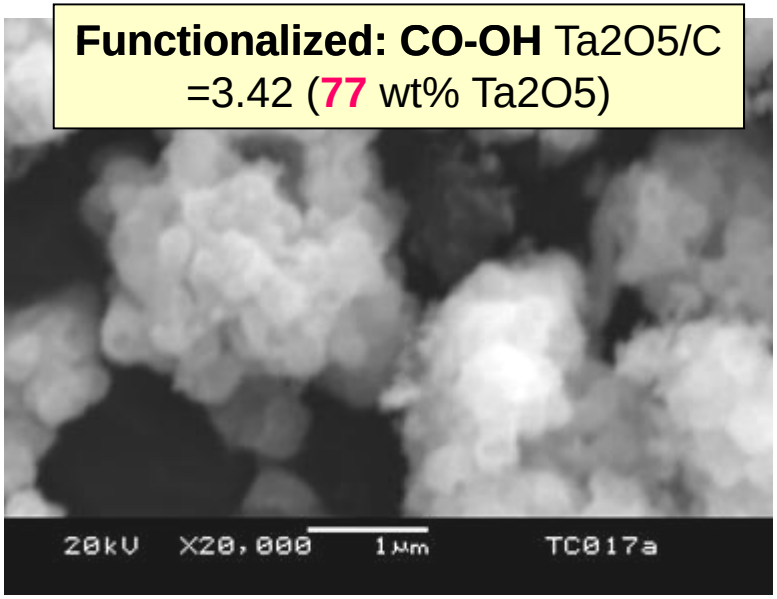
Direct Synthesis: high ratio of Ta_2O_5/carbon (1.71-3.42)

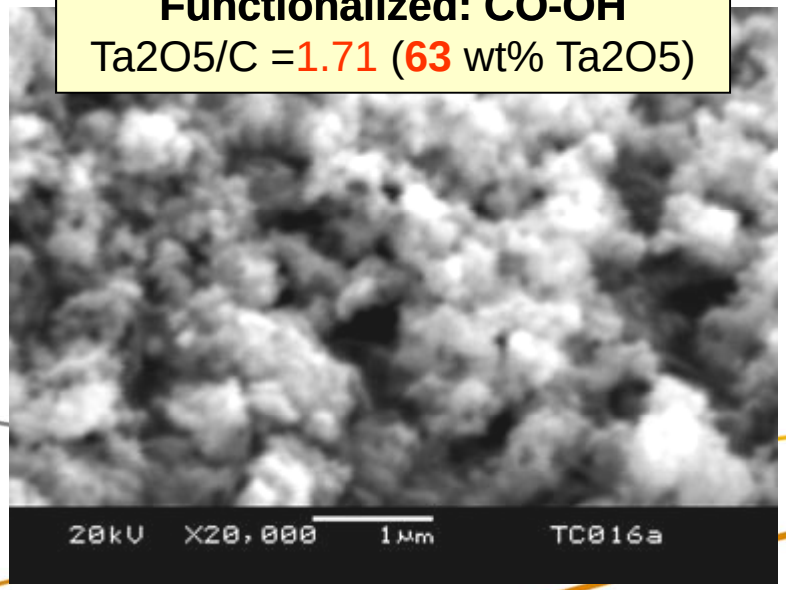
Non-functionalized
Ta2O5/C =3.42 (**77** wt% Ta2O5)



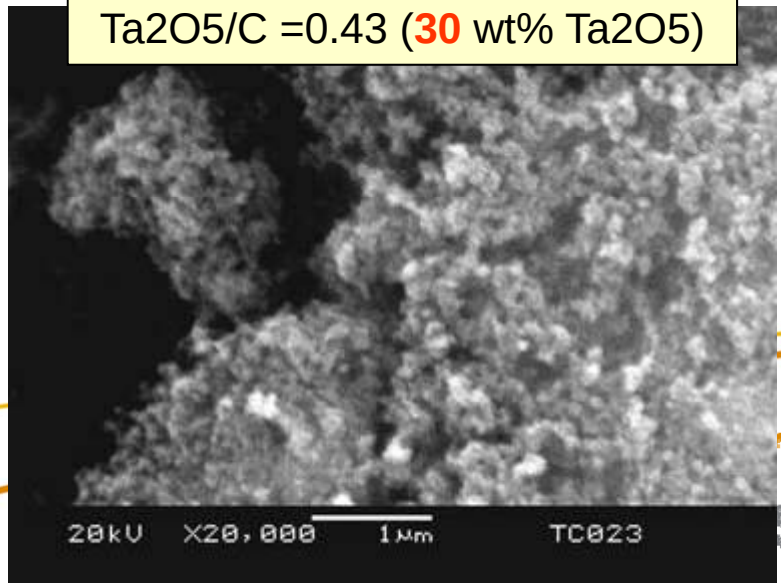
Functionalized: CO-OH Ta2O5/C =3.42 (**77** wt% Ta2O5)



Functionalized: CO-OH
Ta2O5/C =1.71 (**63** wt% Ta2O5)

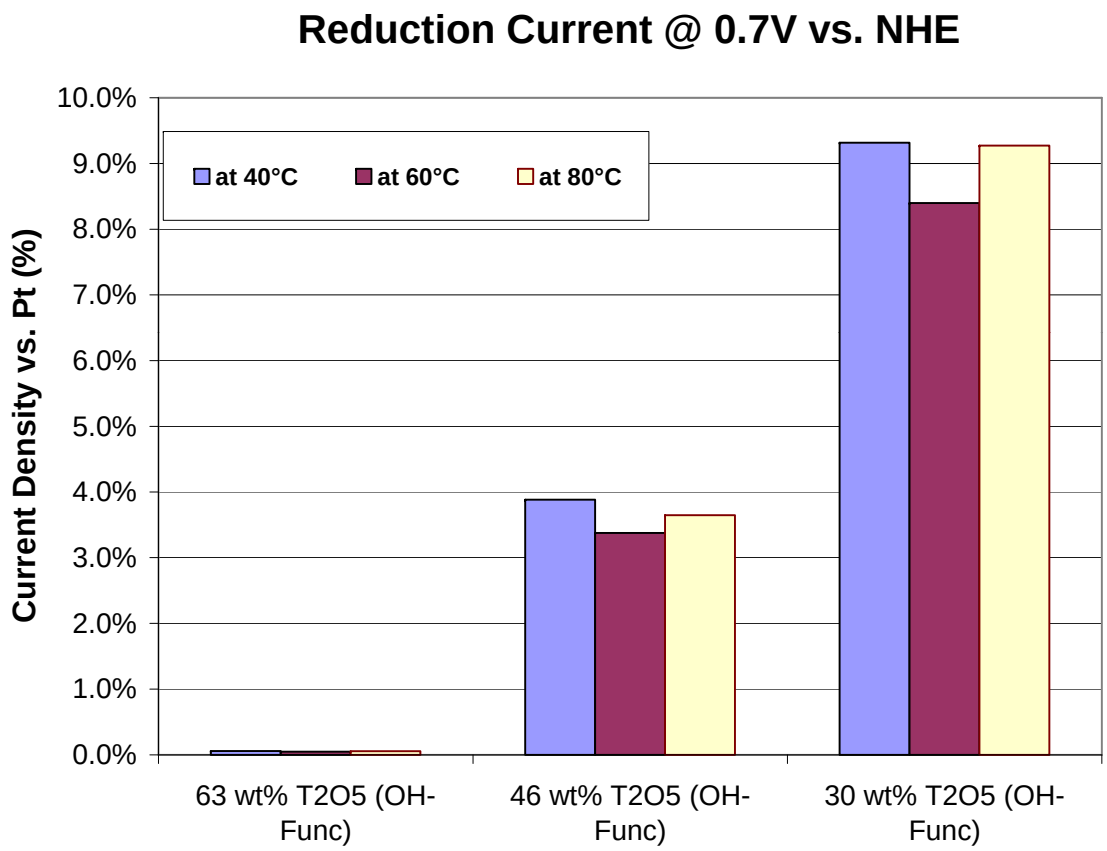


Functionalized: CO-OH
Ta2O5/C =0.43 (**30** wt% Ta2O5)



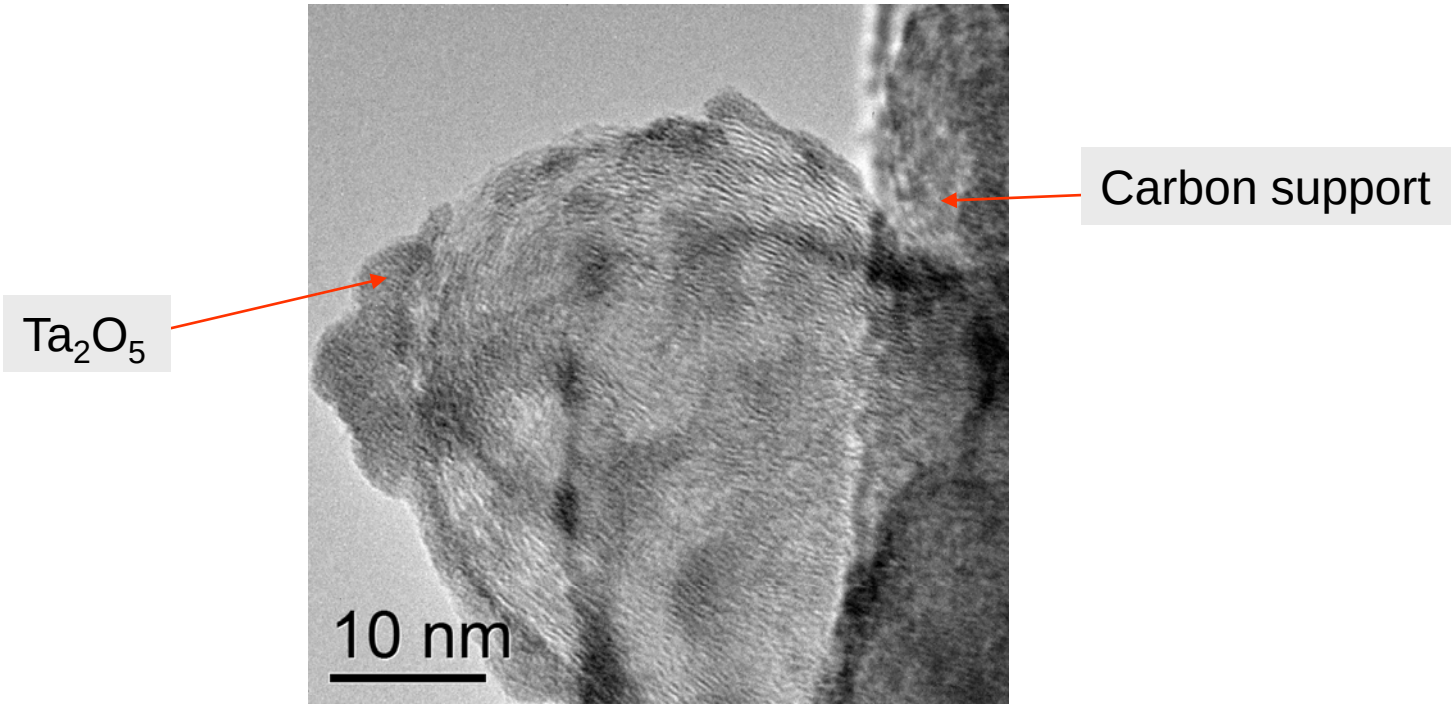
Electrochemical Performance of Ta Oxide

- ***Using a static 3-electrode half-cell setup***



- ***Performance**: Up to 9% of mass specific current density was achieved with 30 wt% Ta oxide @ 0.7V vs. NHE compared to a Pt catalyst (10 wt% Pt on activated carbon).*
- ***Issues**: A high active catalysts loading (30~50 mg/cm^2) and a static electrode can underestimate catalytic activity of Pt due to diffusion limitation*

TEM Study



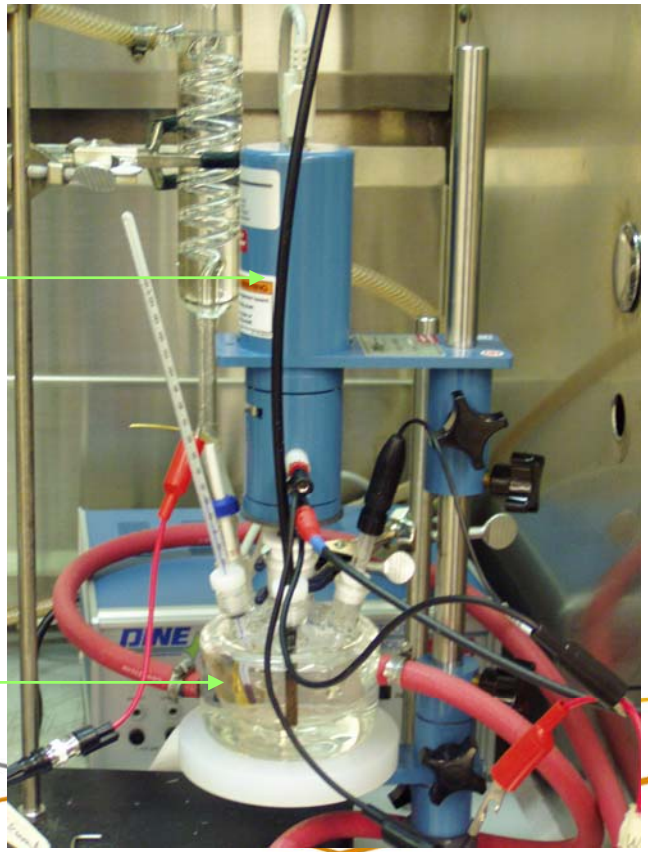
- ***Direct Synthetic Process:*** *A direct reaction between Ta ethoxide and functionalized carbon, which forms covalently bonded nanoscale Ta oxide particles nucleated on the functionalized carbon surface.*
- ***TEM Results:*** *A composite catalyst with 17 wt% Ta oxide prepared using the direct synthesis technique contains well-distributed Ta oxide particles ~20 nm in size.*

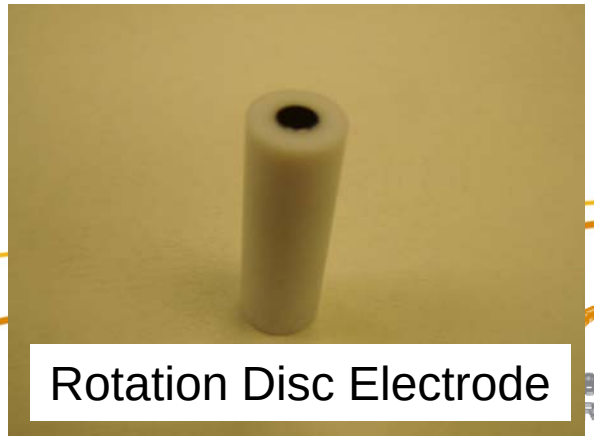
Rotating Disc Electrode (RDE) Test

- **Rotating disc up to 2400 rpm minimizes diffusion limitation from electrolyte to electrode.**
- **Temperature Control Capability**

Electrode Rotator

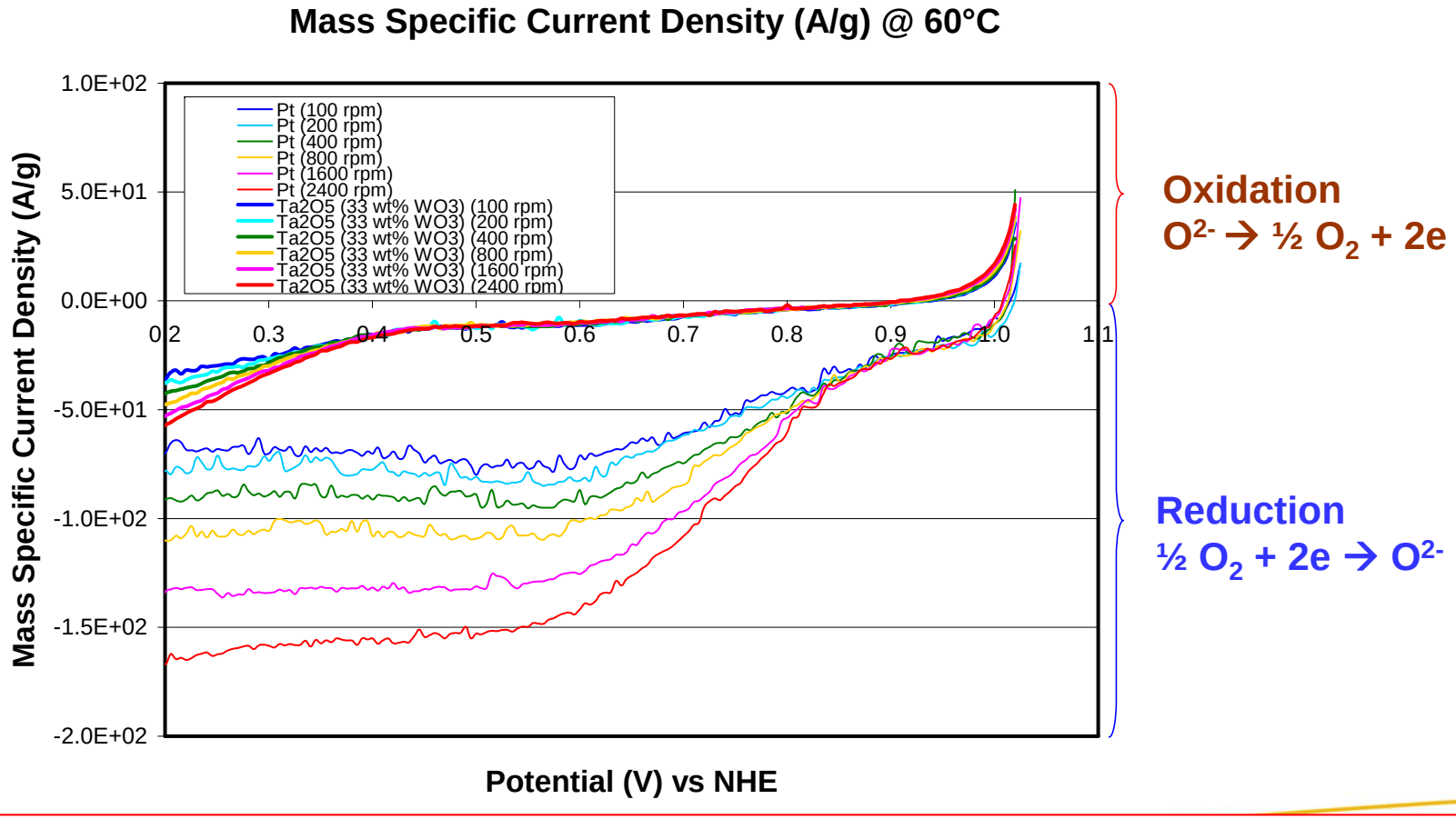
Temperature Controlled Cell





RDE Test Results

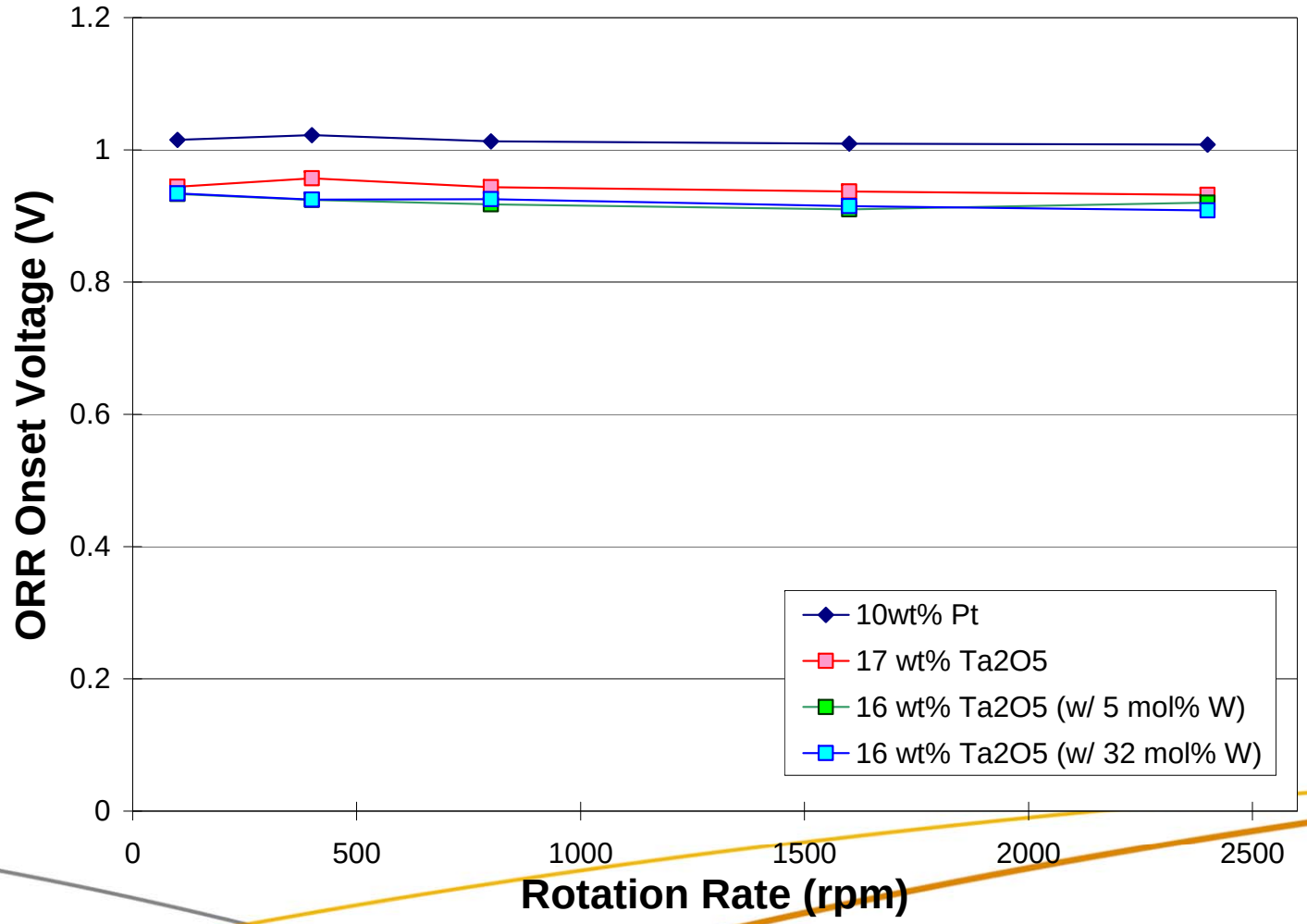
- **Solid loading (Active): ~ 0.2 mg/cm^2**
- **Voltage sweep: 5 mV/sec (1.1~0.2 V vs. NHE) @ 60°C**



- ***Pt:*** *small activation polarization (>0.85V), and diffusion limitation (large change in maximum current density due to rotating speed)*
- ***Nanoscale Ta oxide:*** *large activation polarization (>0.45V), and no diffusion limitation (small change in maximum current density due to rotating speed)*

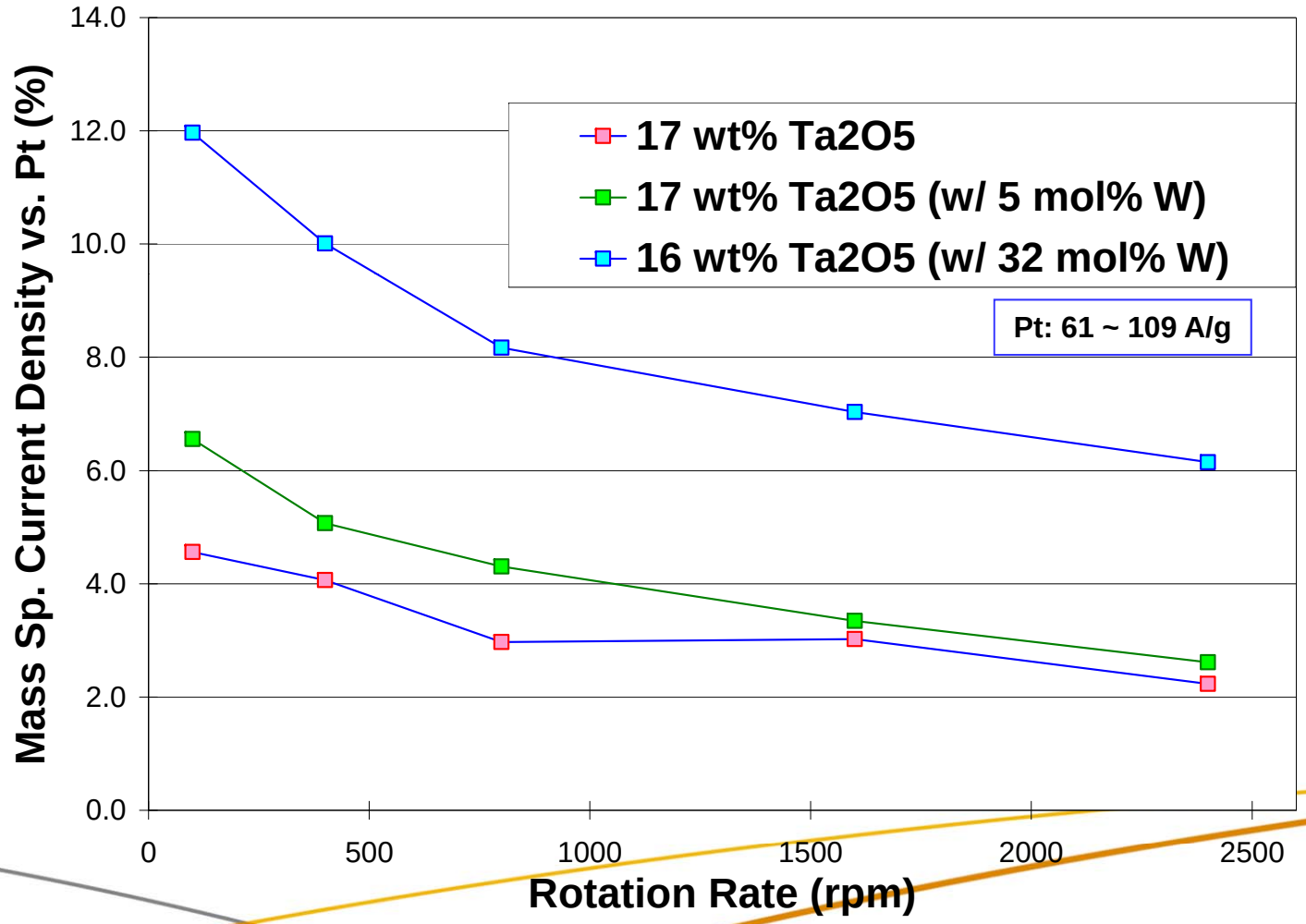
Effects of W Addition To Ta Oxide

- **ORR Onset Potential @ 60°C**



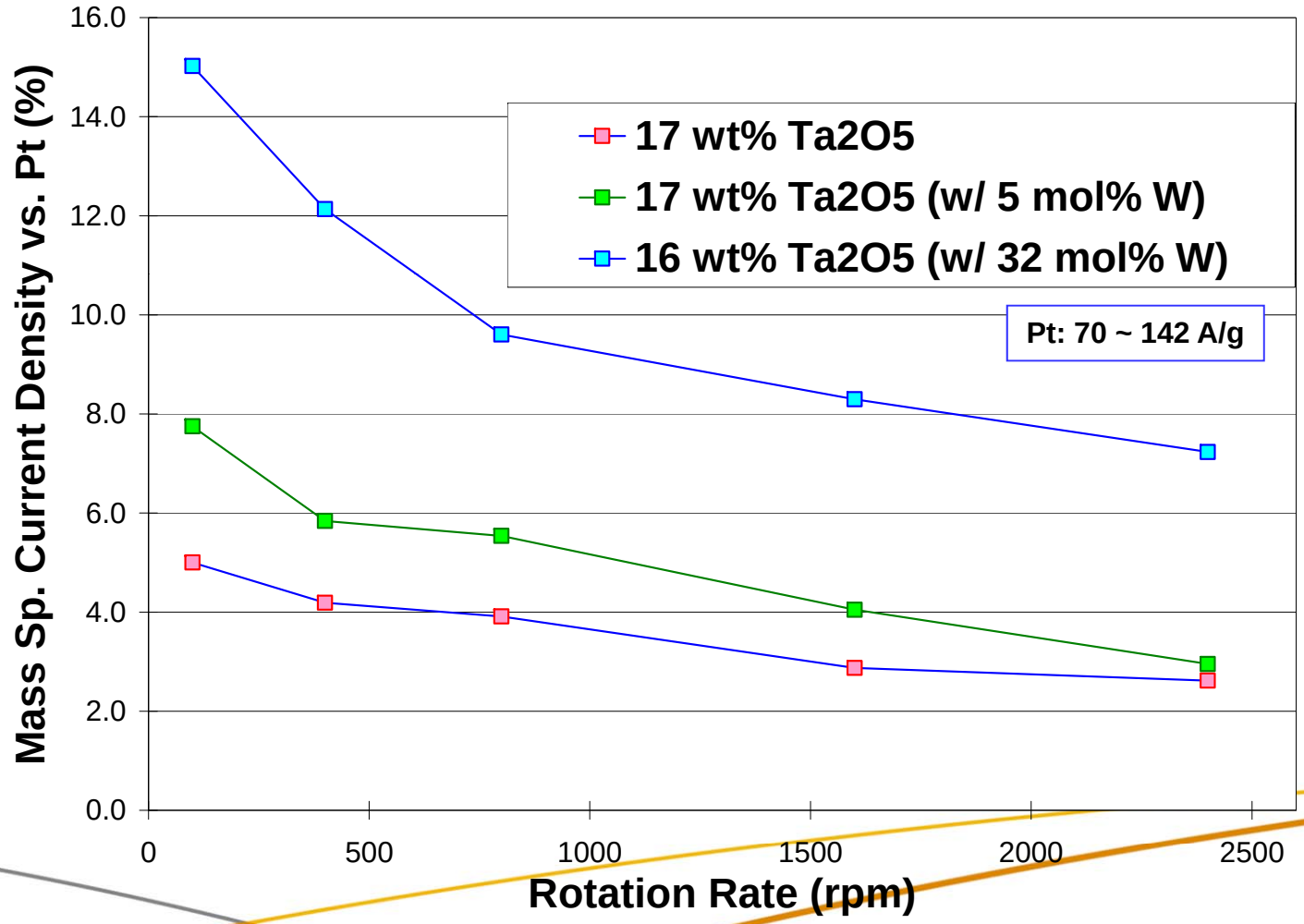
Effects of W Addition To Ta Oxide

- **Mass Sp. Current Density @ 0.7V (60°C)**



Effects of W Addition To Ta Oxide

- **Mass Sp. Current Density @ 0.6V (60°C)**



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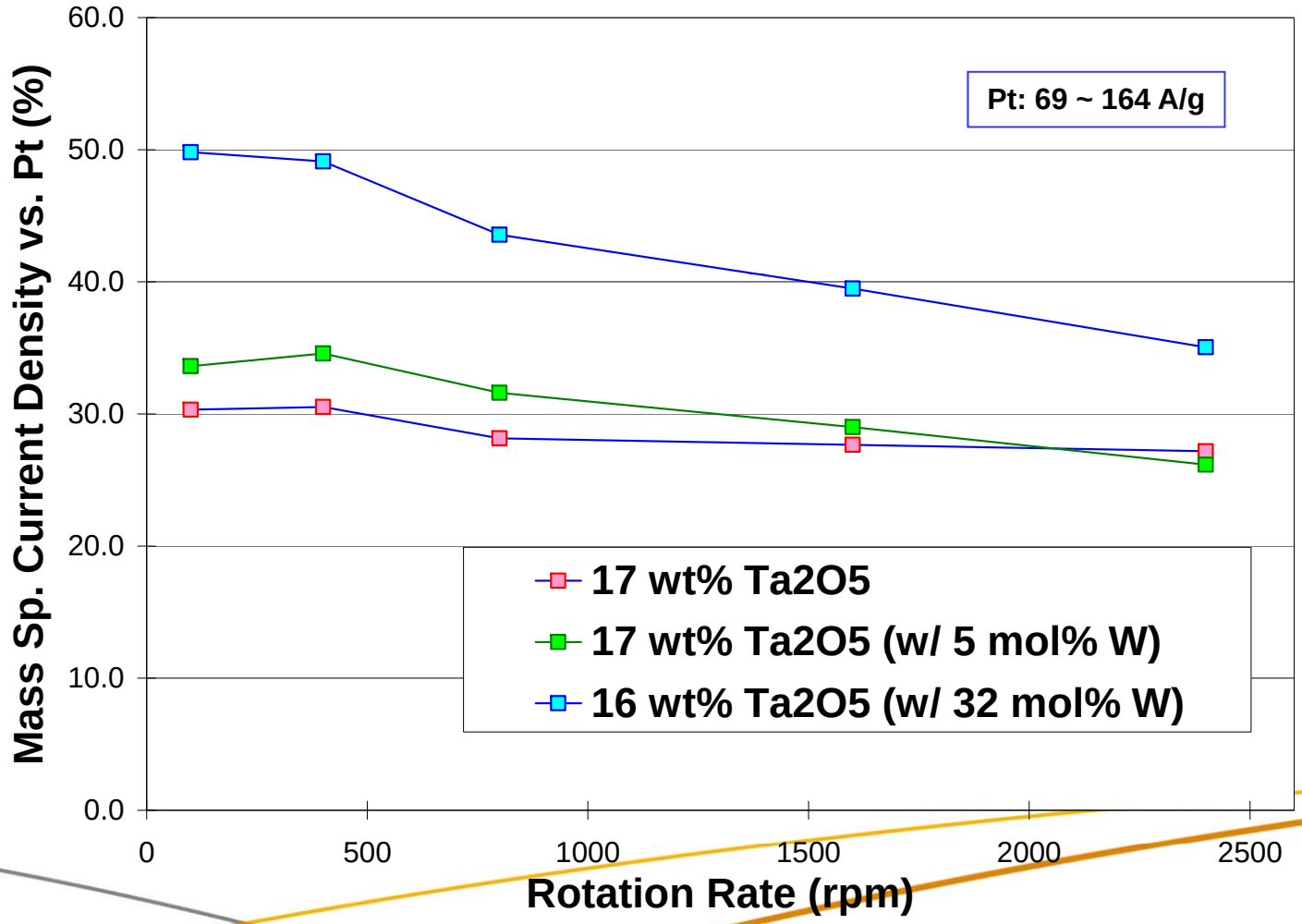
Effects of W Addition To Ta Oxide

- **Maximum Mass Sp. Current Density (60°C)**



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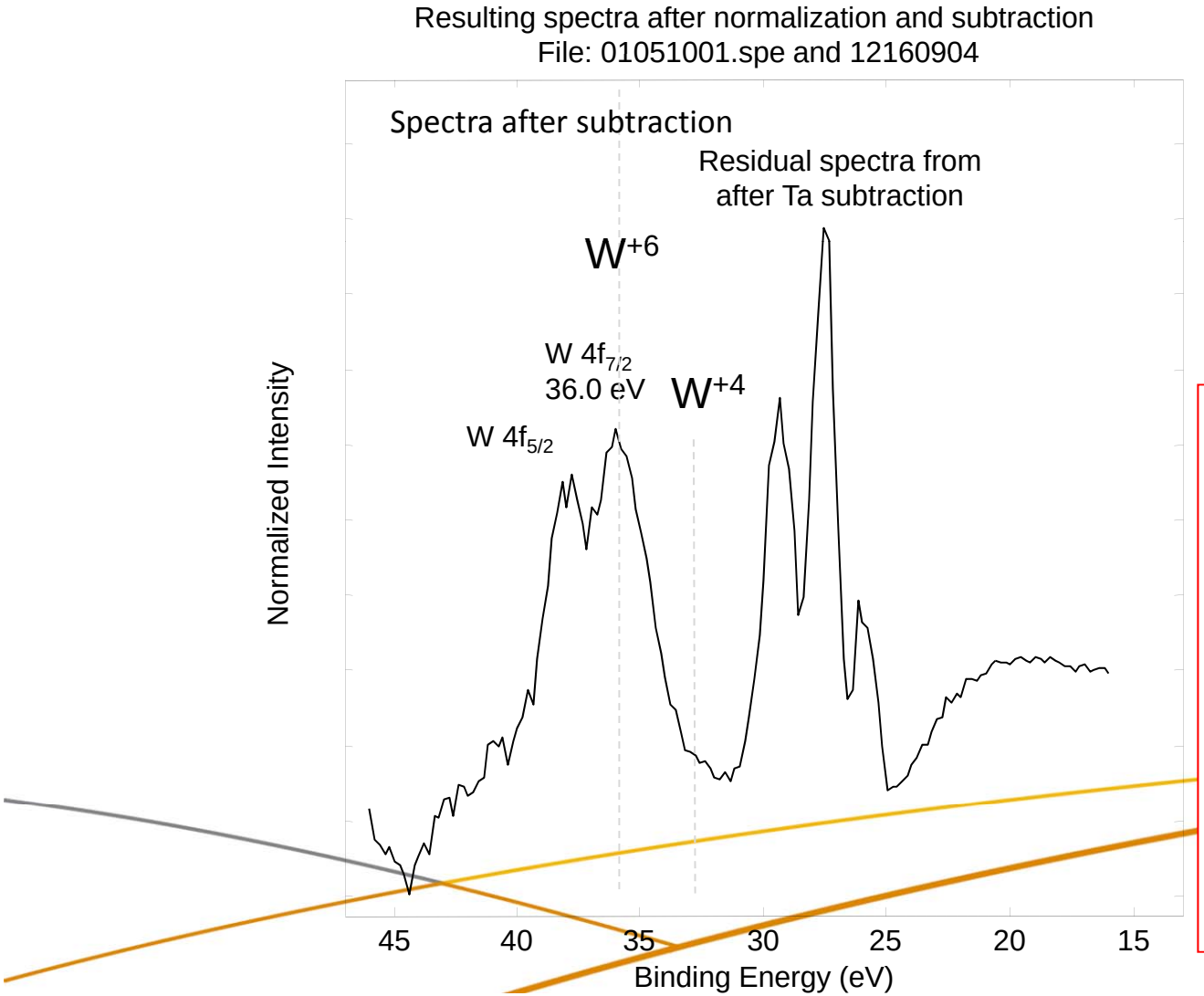
XPS Analysis

- **Ta2O5 with 32 mol% W**

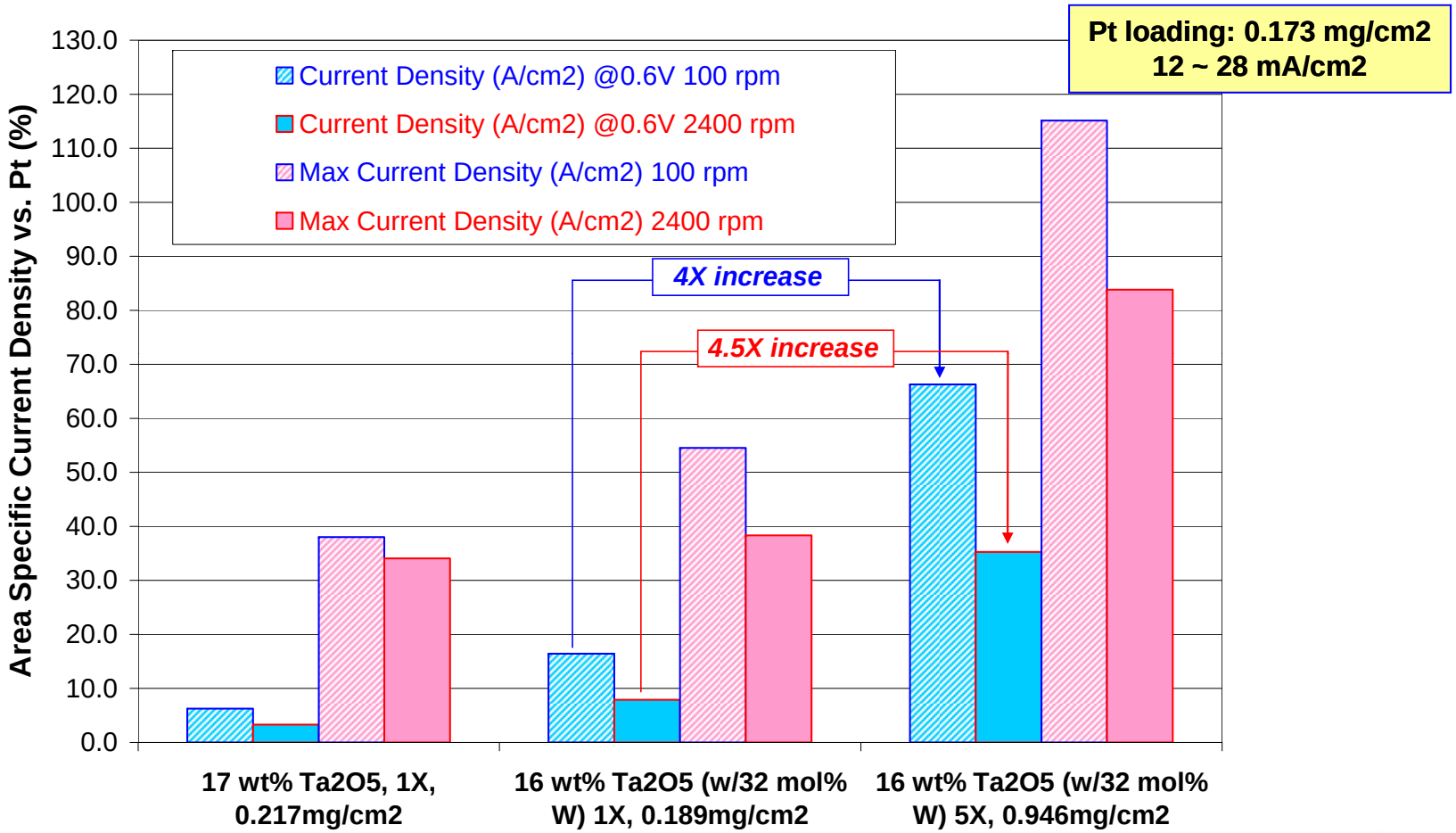
High Energy Resolution Photoemission Spectra of the Ta 4f and Ta 5p Region



- ***A Ta_2O_5 sample with 32 mol% W** shows a peak matched with WO3 (+6: 35.8 eV).*
- *No peak associated with WO2 (+4: 32.8 eV) was observed.*
- *This results indicates W exists as +6 in Ta^{5+}, creating oxygen excess.*

Area Specific Current Density

- **Effect of Catalyst Loading**



- *With 5 times increase in loading of active catalysts, the area specific current density at 0.6V increased 4~4.5 times.*
- *When loaded ~5 times, the composite catalyst with 32 mol% W tested at 0.6V reached 66% at 100 rpm and 35% at 2400 rpm compared to the Pt catalyst.*

Summary

- **Formation of covalent bonding between Ta oxide and functionalized carbon was confirmed by FTIR.**
- **Electrochemical analysis of directly synthesized composites showed significant increase in both mass specific reduction current with decrease in particle size of Ta oxide.**
- **Addition of W to Ta oxide lead to the improvement in catalytic activity of Ta oxide.**
- **The best catalysts with 32 mol% W showed specific current density up to 9% at 0.6V and 35% at maximum current density at 2400 rpm compared to Pt.**
- **XPS analysis revealed that W exists as 6+ in the Ta oxide (5+), indicating the creation of excess oxygen in Ta oxide structure, which improves the improvement of catalytic activity of Ta oxide.**
- **When loaded ~5 times, the composite catalyst with 32 mol% W tested at 0.6V reached 66% at 100 rpm and 35% at 2400 rpm compared to the Pt catalyst.**