

## V.C.10 Tungsten Cathode Catalyst for PEMFC\*

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electrocatalyst targets, specifically activity, cost, and durability.

OSPI Progress Toward Meeting DOE Electrocatalyst Technical Targets

Electrocatalyst Characteristic	Units	2005 Target	OSPI tungsten catalyst status
Cost	\$/kW	40	<10
Durability	Hrs at T<80°C	>2,000	3,200
Non-Pt catalyst activity/volume	A/cm <sup>3</sup> at 800mV	50	16

### Accomplishments

- Completion of fundamental studies of the tungsten catalyst electro-synthesis. Electrochemical reduction leads to an electronic and structural change of the ammonium metatungstate molecule, resulting in a decrease in the distance between W atoms in the W<sub>3</sub>O<sub>10</sub> triplets of the Keggin structure.
- Optimization of the ammonium metatungstate precursor catalyst composition, yielding improved performance. Performance validation at Los Alamos National Laboratory (LANL) in November 2005 confirmed a 2.5x improvement of the Type II material over the initial (Type I) ammonium metatungstate catalyst performance.
- Demonstrated a catalyst activity/volume of the Type II catalyst material of 16 A/cm<sup>3</sup> at 800 mV.
- Demonstrated durability of the Type II catalyst with load cycling over 3,200 hrs. The activity/volume of the Type II catalyst maintained 16 A/cm<sup>3</sup> at 800 mV throughout the 3,200 hours of load cycling.

### Objectives

- Evaluate current non-precious metal, tungsten catalyst in cathode applications.
- Optimize catalyst synthesis to achieve an activity improvement towards attaining the DOE technical target for non-platinum catalysts.
- Demonstrate catalyst durability with load cycling at initial performance, at 250 hours, and over 1,000 hours.

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Cost
- (C) Electrode Performance

### Technical Targets

This project performs fundamental and applied studies of tungsten cathode catalysts. Insights gained from these studies will be applied toward the design and synthesis of catalyst materials that meet the DOE 2010

### Introduction

The commercial viability of fuel cell technology has been hindered, at least in part, by the high cost of catalyst materials. Current state-of-the-art, low temperature fuel cells employ platinum catalysts, which account for a significant portion of the overall system cost. Addressing this issue by developing non-precious metal materials that can equally perform the electrocatalysis would facilitate the implementation of fuel cell technology.

To this end, OSRAM SYLVANIA has developed a tungsten material which shows catalytic activity for fuel cell applications. Tungsten is more abundant than platinum, and thus, historically its metal ore cost has

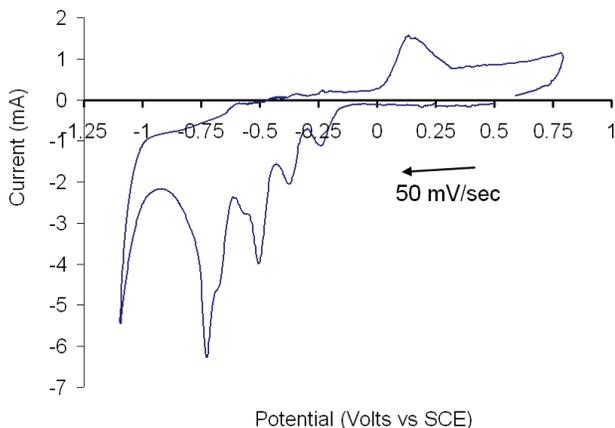
been, and continues to be, several orders of magnitude lower than platinum. Initial tests have shown that upon electrochemically synthesizing this tungsten-based catalyst, its activity as the cathode in a fuel cell reaches 5 to 25% of a comparable mass loading of platinum. More recently, the efforts outlined here have focused on optimizing the catalysis synthesis and precursor composition, with the goal of improving the tungsten-based catalytic activity. Successful optimization of these materials can contribute to the DOE's technical targets for electrocatalysts by minimization of the overall MEA cost, all the while preserving the peak efficiency that such systems can offer.

## Approach

This project focuses on optimization of an all-tungsten electrocatalyst previously discovered and verified as active for both the PEM cell anode and cathode. In initial cathode operation studies, the tungsten-based catalytic activity performed below the status reported in the DOE Multi-Year Research, Development and Demonstration Plan for non-Pt catalyst activity. This work will aim to build a greater understanding of the activation process and its products, leading to new precursor materials and activation procedures that will likely yield major improvements in catalytic activity over the initial work.

## Results

The metatungstate Keggin structure comprises four  $W_3O_{10}$  triplet "caps" which surround a central cavity containing two protons. In acid electrolyte, metatungstate can undergo multiple reductions by up to 24 electrons, as shown in Figure 1, while maintaining its structural integrity. The initial stages of the reduction

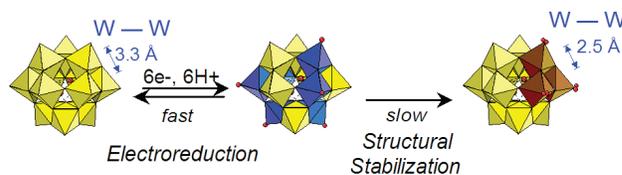


**FIGURE 1.** Cyclic Voltammogram of Electroreduction Scheme of  $Na_6[H_2W_{12}O_{40}]$  Precursor Material

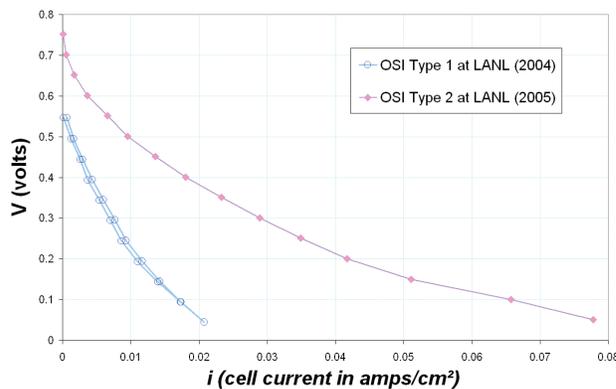
pathway of metatungstate, as shown in Figure 2, involve a relatively fast and reversible reduction by six electrons, delocalized throughout the structure, along with the incorporation of six protons. A slower chemical step following the electrochemical reduction yields a stabilized structure, in which all six electrons localize to one of the four  $W_3O_{10}$  caps, resulting in the distance between the tungsten atoms within the cap to change from 3.3 Å to 2.5 Å. It is this latter structure, which offers both an electronic and structural modification of the initial material that is believed to act as a catalyst.

The above finding is significant in that it dictates that the catalyst not only be electrochemically reduced, but also be allowed to "condition" in order to form the structurally stable species. Recent efforts have focused on optimizing the composition of the precursor material to minimize hydration and solubility, leading to a more stable catalyst structure in the membrane electrode assembly (MEA). A Type II catalyst was thus prepared based on hydration improvements. Testing demonstrated its activity improved by over 2x compared to the initial catalyst, as shown in Figure 3 for a validation experiment performed at LANL.

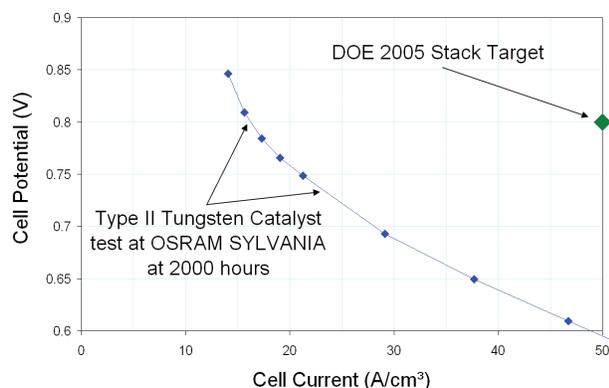
The performance of the Type II catalyst material also performed better at higher voltages, which is required for high efficiency operation in order to meet cost and packaging requirements. Figure 4 shows the



**FIGURE 2.** Structural Rearrangement of Polyoxometalate after Electroreduction (ref. 1)

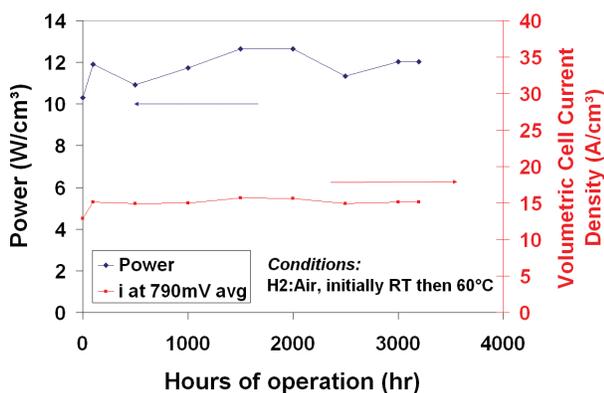


**FIGURE 3.** LANL Test Data for Type I (2004) and Type II (2005) Catalyst



**FIGURE 4.** Performance Curve of Type II Catalyst During Long-Term Testing

activity between 800 and 600 mV in terms of activity/volume of catalyst, based upon a 10  $\mu\text{m}$  thick catalyst layer, revealing the improvement towards the DOE 2005 technical target of 50  $\text{A}/\text{cm}^2$  at 800 mV. Moreover, as shown in Figure 5, the durability of this catalyst when subjected to load cycling remains constant for over 3,000 hours.



**FIGURE 5.** Type II Catalyst Single Cell Performance at 800mV over 3,200 Hour Life Test

## Conclusions and Future Directions

Fundamental studies towards the electrochemical reduction of metatungstate revealed the conditions under which it undergoes an electronic and structural change, likely leading to a catalytic species. Through the optimization of the precursor composition of the metatungstate species to yield a more durable cathode electrocatalyst, the activity of the tungsten-based cathode catalyst improved over 2x from the initial catalyst species. While falling short of the 2005 DOE technical target of 50  $\text{A}/\text{cm}^2$  at 800 mV, its durability exceeded the technical target of 2,000 hours. This first optimization of the precursor composition provided the means for this significant enhancement towards meeting the 2005 DOE technical targets. Future work will continue to focus on the optimization of the activation conditions and precursor composition in order to meet the 2010 DOE technical targets for electrocatalysts, while also demonstrating the feasibility of a non-precious metal, all tungsten anode and cathode fuel cell.

## FY 2006 Publications/Presentations

- Christian, J.; Mendenhall, R.; Smith, S.; Gingerich, R.; Lunk, H-J.; Dang, T. *Tungsten Cathode Catalyst for PEM Cells*, 2006 DOE Hydrogen, Fuel Cells Infrastructure Technologies Program Review, 17 May 2006.

## References

- Jeannin, Y, et al., *Inorganic Chemistry*, 1980, p. 2933.