

2006 DOE Hydrogen Program Merit Review And Peer Evaluation Meeting

Electrocatalyst Supports and Electrode Structures

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This presentation does not contain proprietary or confidential information.

FC 21

Project Overview

Electrocatalyst Supports and Electrode Structures

Timeline

- “Started” FY04
- End date not established
- 50% Complete

Barriers

- B. Cost
- C. Electrode Performance
- A. Durability?

Budget

- 100% DOE
- Total FY05 = \$800k
- Total FY06 = \$800k

Partners

- Radoslav Adzic and co-workers (BNL)
- Karren More (ORNL)
- LANL: T-12 (Theoretical Physics), MST-8 (EXAFS)

Project Objectives

■ Objectives:

- Reduce the amount of Pt required (Technical Targets below).
- Improve Pt catalyst stability/durability (compared to carbon supports).
- Improve electrode manufacturability and performance.

Technical Targets (Tables 3.4.13 & 3.4.14)			
Characteristic	Units	Targets (Stack)	
		2010	2015
PGM* Total Content (Electrocatalyst TT)	g/kW (rated)	0.5	0.4
PGM Total Loading (Electrocatalyst TT)	mg PGM/cm ² electrode area	0.3	0.2
Total Catalyst Loading (MEA TT)	g/kW (rated)	0.33	0.2

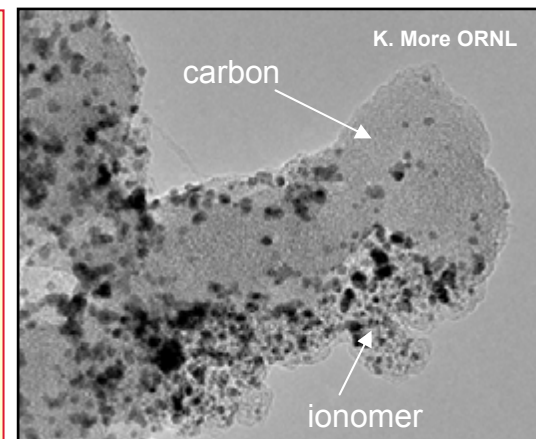
*PGM - Platinum group metal

Objectives - The need for new Pt support materials

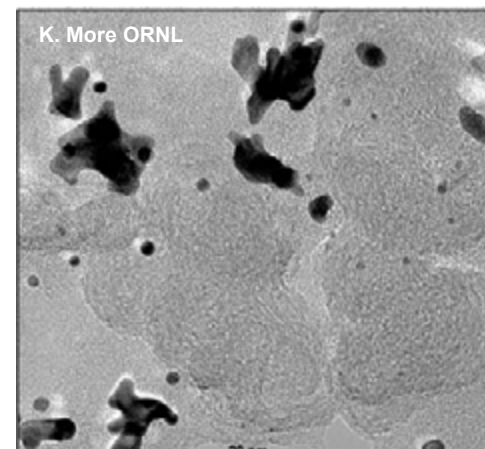
■ Current FC catalysts typically consist of Pt nanoparticles on carbon black supports. Several problems with Pt/C catalysts are:

- No “adhesion” between Pt and C
 - particles lost to ionomer (top SEM),
 - also particle growth by coalescence.
- Particles are more susceptible to dissolution particle growth (lower SEM),
- Highly dispersed Pt particles are inactive on a passive support.

■ In order to achieve low Pt-loadings and durability, supports are needed that can stabilize highly dispersed Pt, yet provide an environment that enables bulk-like activities.



Pt particles lost to the ionomer.



Pt particle growth from 1.2 V cycling.

Approach

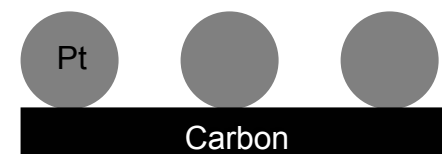
“Stabilize” highly dispersed Pt catalysts using “interactive” supports

1) Use Group VIII type supports (BNL catalysts).

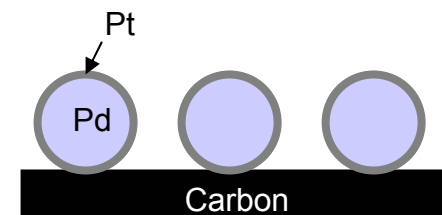
- Replicate a Pt-like substructure and electron environment.

2) Use electropositive supports that “compensate” the Pt.

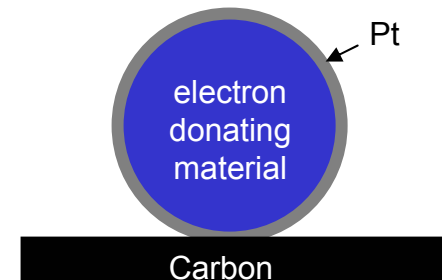
- Donate electrical charge to electron-deficient sub-crystalline structures.
 - Facilitates oxygen reduction process.
 - Forms dipole at interface.
 - Improves wetting /adhesion.
- Investigate low work function materials.
 - Work functions indicate relative ease of removing electrons from a surface.



Conventional Catalyst



BNL Catalyst



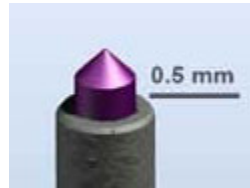
Ceramic Supported Catalyst

Work Function: Simplistic Explanation of Relevance

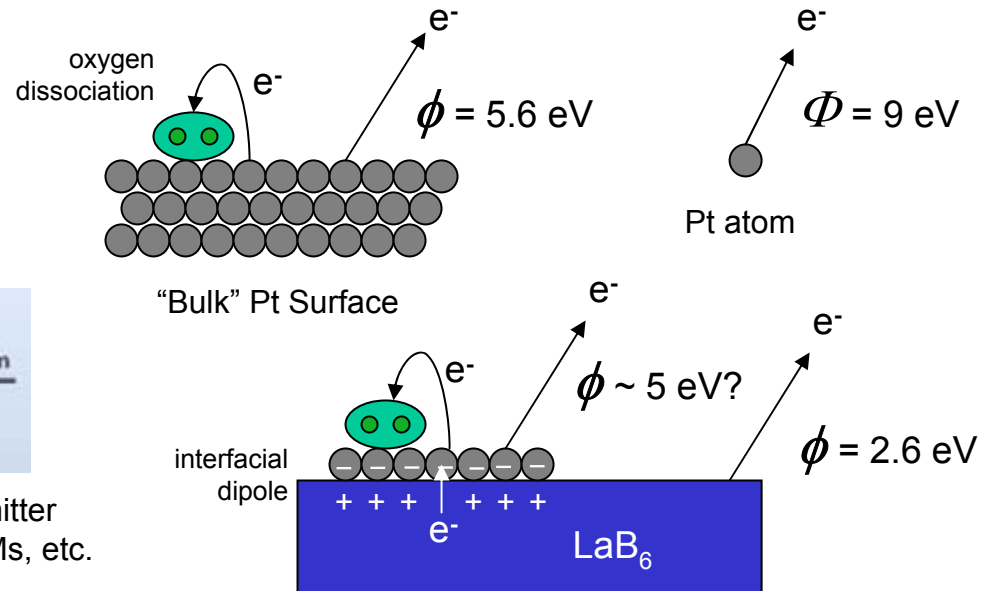
Material **Work Function**
 ϕ (eV)

B	4.5
C	5.0
La	3.5
LaB ₆	2.6
Pd	5.2
Pt	5.6
W	4.5

From CRC



LaB₆ thermionic emitter
used in SEMs, TEMs, etc.



Work Function: energy to move e^- from Fermi level to infinity

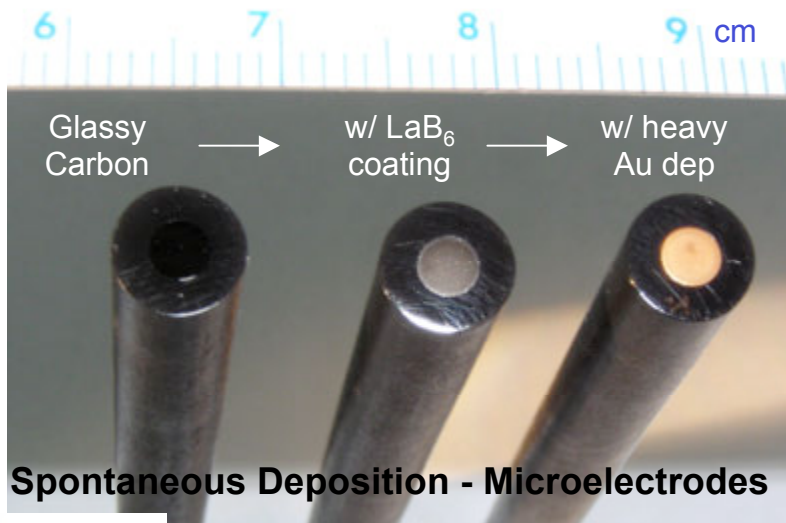
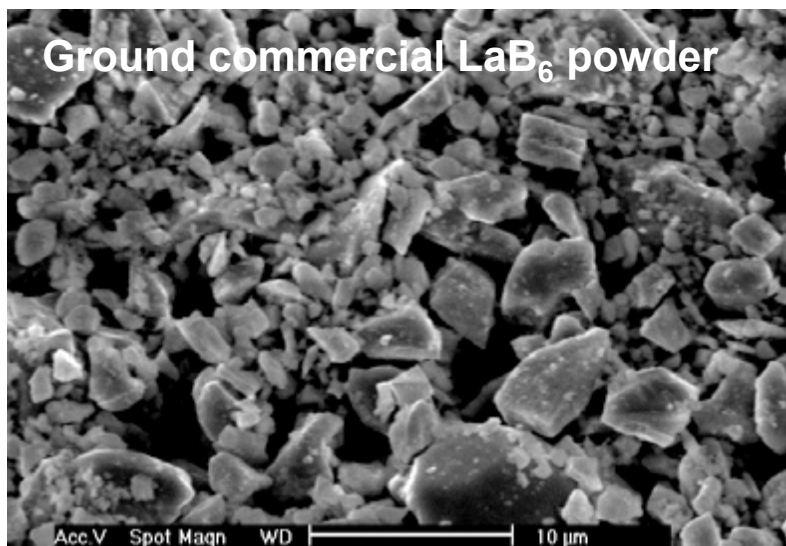
Caveats: ϕ 's are "ideal" vacuum condition values (no contaminants), and
 ▪ catalysis involves far more than highest electron energies.

Low Work Function Materials used as Thermionic Emitters

- Hexaborides:
 - Good conductivities and resistant to acids.
- Low ϕ Oxides (BaO, SrO, CaO...):
 - Poor conductivities and acid (or water) soluble.
- Low ϕ Nitrides and Carbides (TiC, ThN...):
 - Best ϕ 's > 1 eV higher than best oxides, hexaborides

Best Choice: Hexaborides

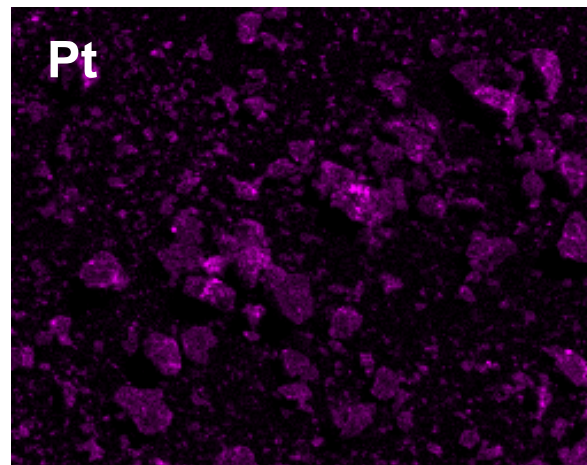
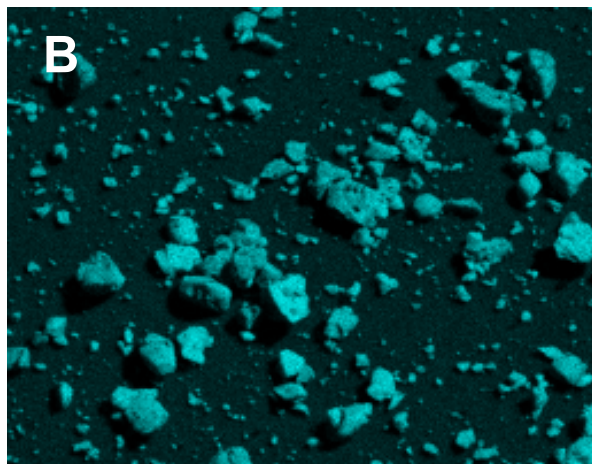
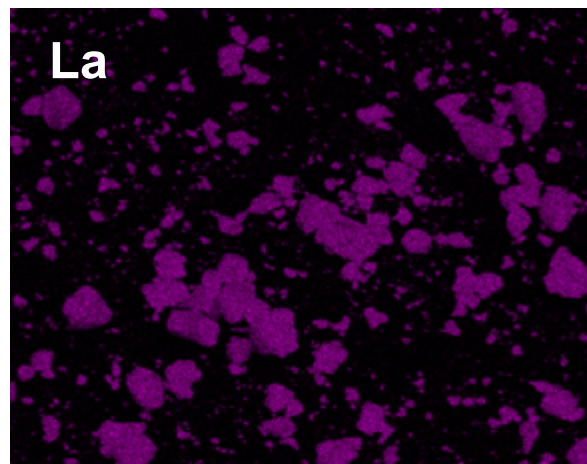
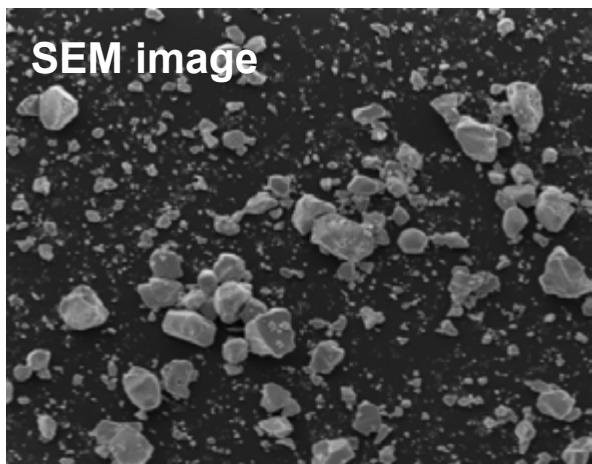
Bonus: Spontaneous Deposition with Hexaborides



■ Hexaboride materials support spontaneous deposition.

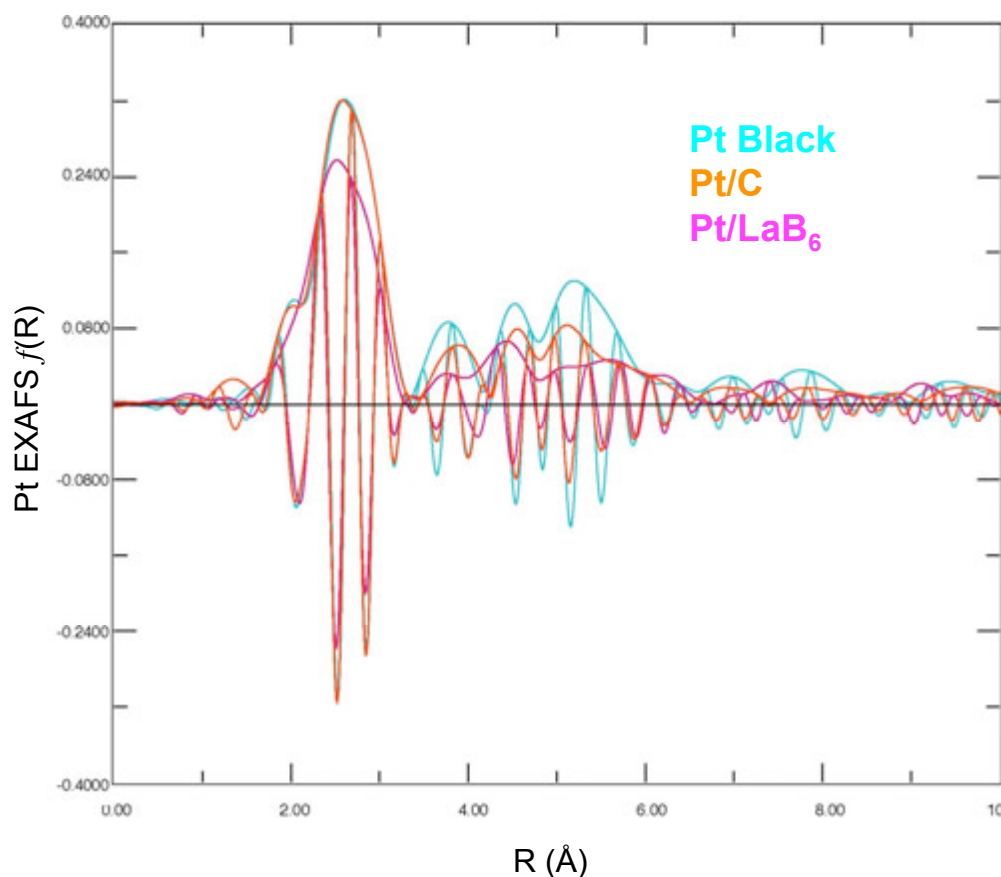
- So far have shown w/ La, Y, Ce, Ca, Gd and Eu hexaborides.
 - probably works with all the lanthanide hexaborides
- Spontaneously deposits Pt, Pd, Au, Ag, Rh,
- Catalyzation process:
 - Add solution.
 - Deposits in seconds.
 - Dry, rinse, or use as is.
- Deposition properties:
 - Very uniform depositions
 - “Subcrystalline” easily achieved (per XRD)
 - Thick also possible

EDAX mapping of Pt deposited on LaB_6



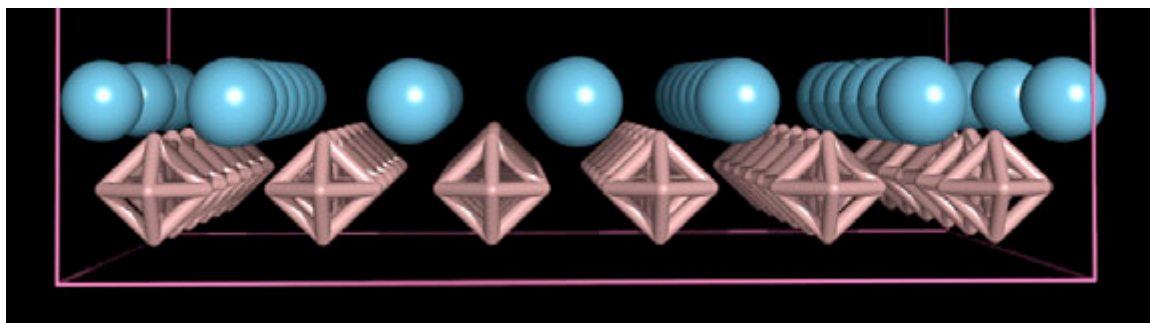
After spontaneous deposition of Pt on disk electrode
with loadings of $150 \mu\text{g LaB}_6/\text{cm}^2$, $5 \mu\text{g Pt}/\text{cm}^2$

Preliminary EXAFS Results (MST-8) (extended x-ray absorption fine structure)

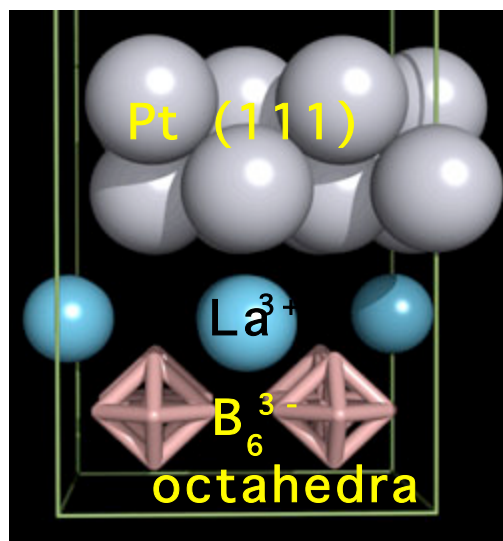


- Analyses have been performed on Pt-black, Pt/C and Pt/LaB₆ materials to compare the nature of the Pt bonds.
 - Curves suggest that Pt is in 2-D (sheet) on Pt/LaB₆ rather than 3-D (cluster) as with Pt/C and Pt black.
 - Nature of Pt/LaB₆ interaction not clear, (structure model and analyses required), but Pt in Pt/LaB₆ clearly different than in Pt/C.

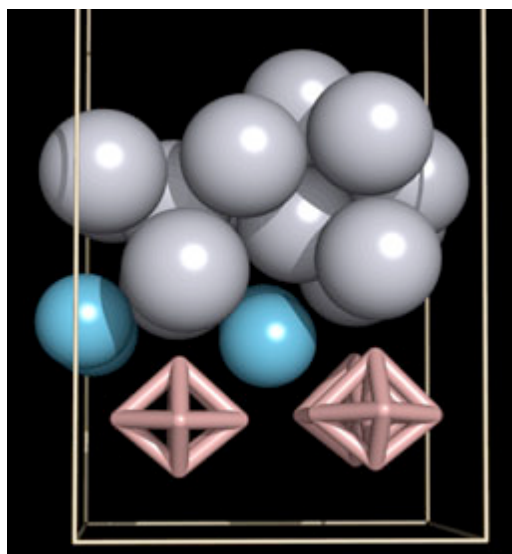
Modeling of Supports (T-12)



LaB₆ model surface used for simulations

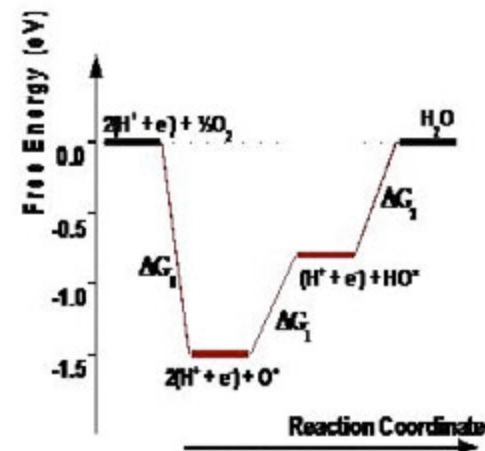


Starting Model



Optimized Model

Simulations of a Pt “bilayer” on an LaB₆ surface



Free energy reaction coordinate for oxygen reduction on Pt(111).

↑ Oxygen reduction calcs using Nørskov approach [(*J. Phys. Chem. B*, 2004) 17886-17892].

← Structure calcs performed using periodic density functional theory calculations in a plane wave basis with ultrasoft pseudopotentials as implemented in the VASP (Vienna Ab Initio Simulation Package) software.

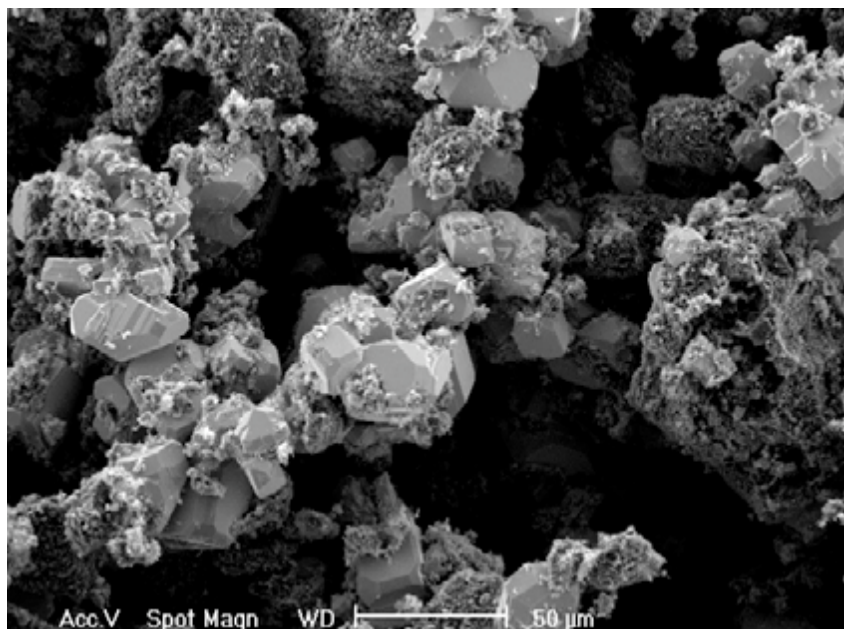
■ Combine the two to model ORR on Pt/hexaboride

■ Introduce oxygen

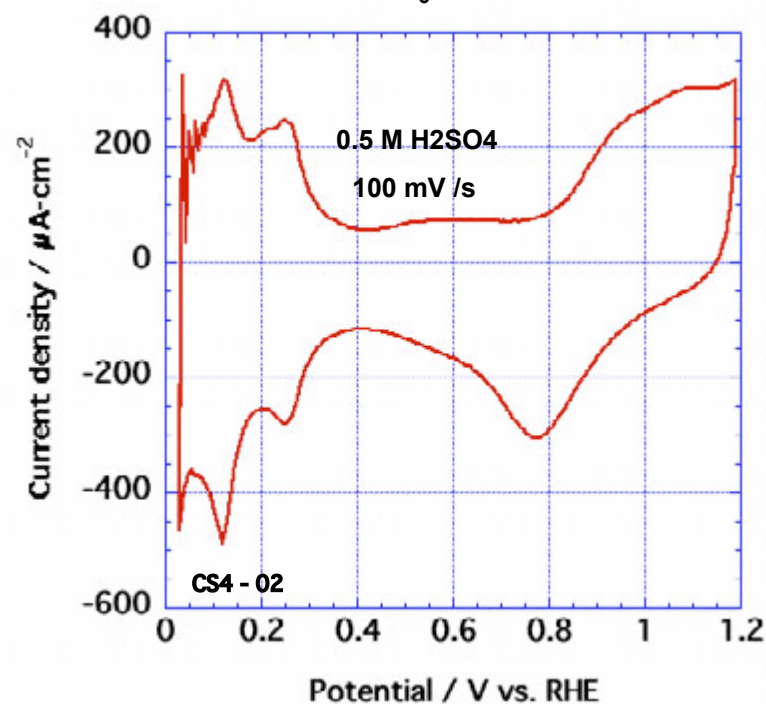
Half-cell results with Low Surface Area EuB_6

Calculated ϕ s: $\text{BaB}_6 < \text{CaB}_6 < \text{EuB}_6 < \text{LaB}_6 < \text{CeB}_6 < \text{YB}_6$ Rep. Prog. Phys. **69** (2006) 181-232

SEM of EuB_6 before Pt deposition



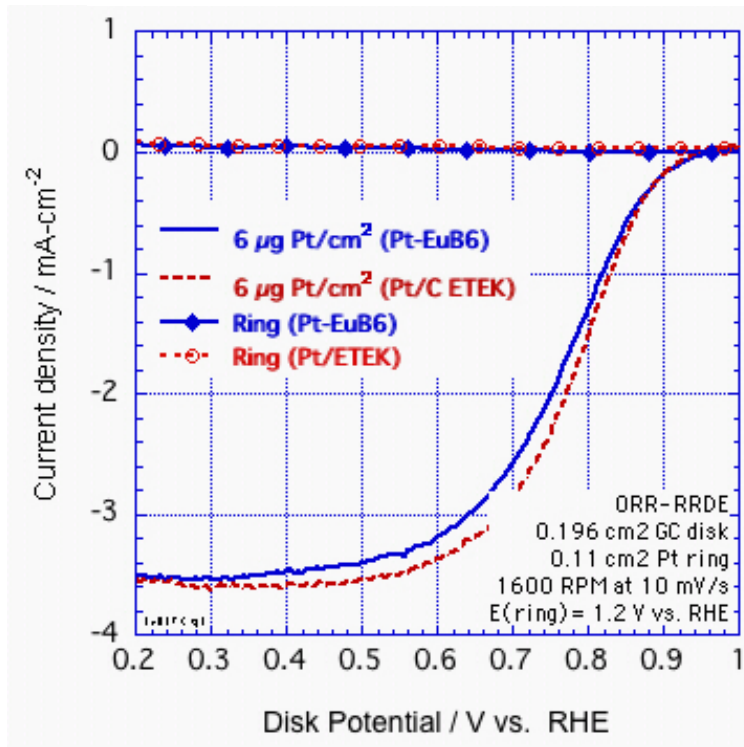
CV of a 4wt%Pt/ EuB_6 film in acidic media



- Predominantly large “gems” of crystalline EuB_6 as synthesized.
- Surface area at most 1 m^2/g (BET).
- Highest Pt utilization yet on B_6 materials (Pt EC active area = 39 m^2/g Pt).
- At 4 wt%, Pt surface area is > than EuB_6 surface area.
 - Full coverage would require ~ 1.2 nm thick Pt film
 - Pt spheres would be ~ 7 nm diameter and cover 40% of the EuB_6 surface

RRDE results with Low Surface Area Hexaborides

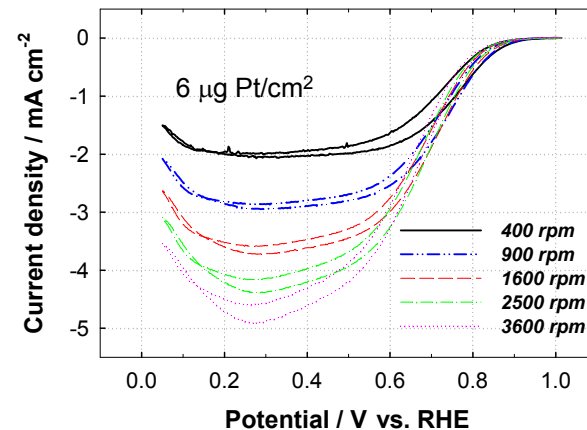
RRDE comparisons of Pt/EuB₆ and Pt/C



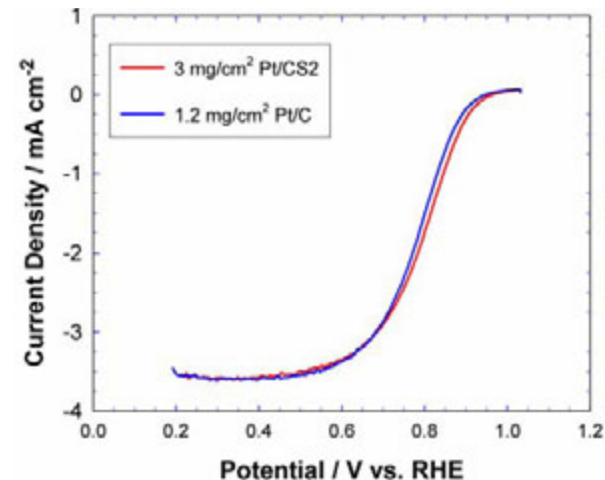
- Pt/EuB₆ close to replicating Pt/C
- Pt/YB₆ possibly equivalent
- Pt/LaB₆ not as good

Note: surface areas are different

CVs of Pt/LaB₆ powder using RRDE
 in O₂-saturated acidic media

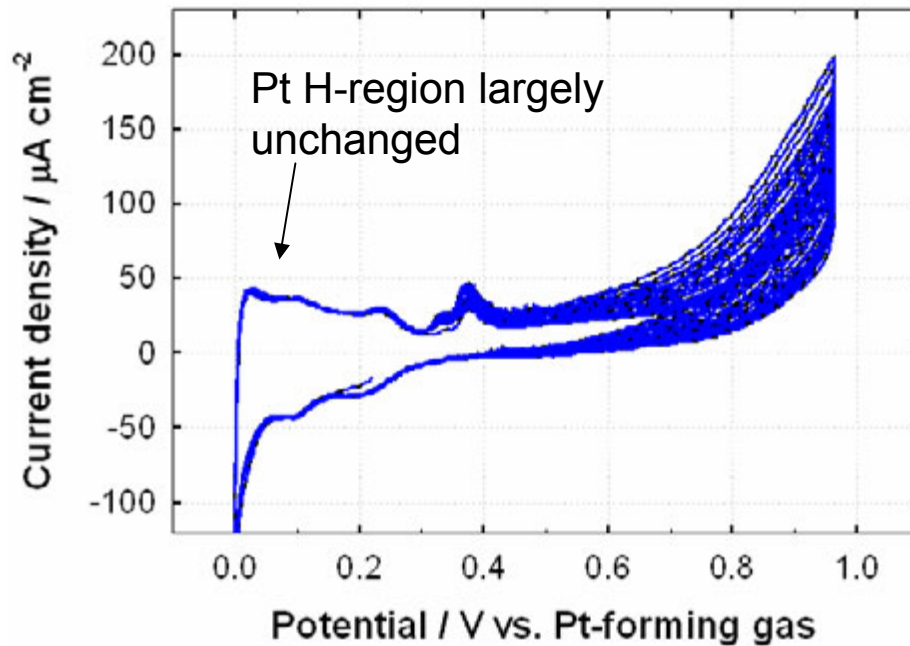


RRDE comparisons of Pt/YB₆ and Pt/C



CVs of Pt/CaB₆ powder

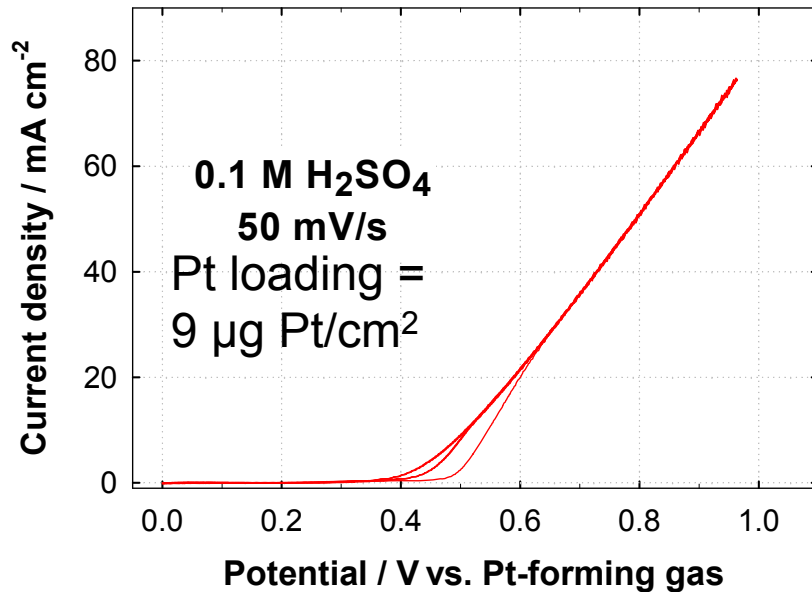
CV of Pt/CaB₆ powder in acidic media



- With multiple cycles, CaB₆ support dissolves away, leaving Pt behind.
- Not unexpected, since CaB₆ is attacked by acid.

Single Crystal Studies on LaB_6 surfaces

CV of Pt/ $\text{LaB}_6(100)$ in acidic media

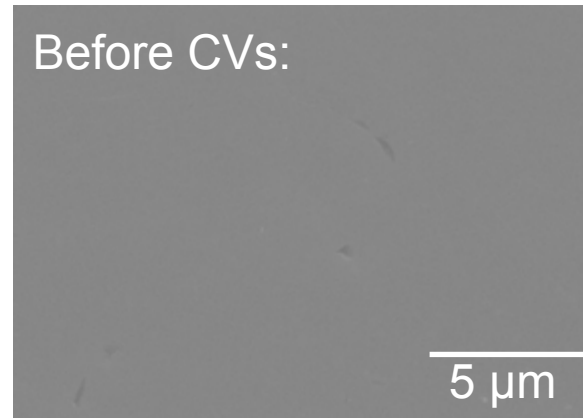


Massive support degradation

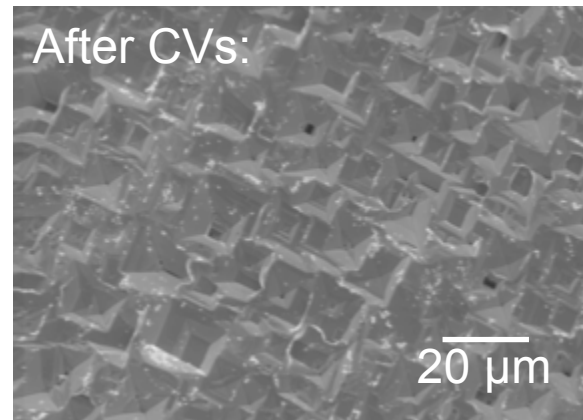
- CVs and degradation effects are the same w/ or w/o Pt
- Similar effect observed on $\text{LaB}_6(310)$ and $\text{LaB}_6(110)$
- CeB_6 single crystals behave similarly

SEMs of $\text{LaB}_6(100)$ surfaces

Before CVs:

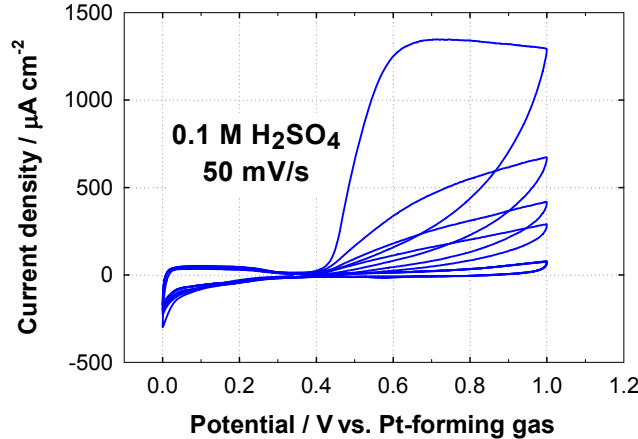


After CVs:

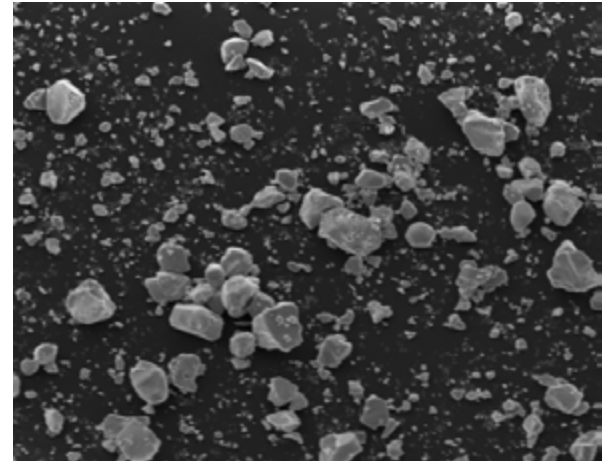


Crushed single crystal powders quickly stabilize

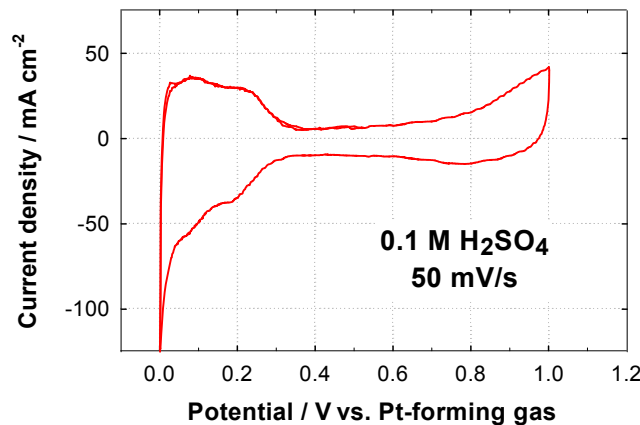
Initial CVs of Pt/LaB₆ powder in acidic media



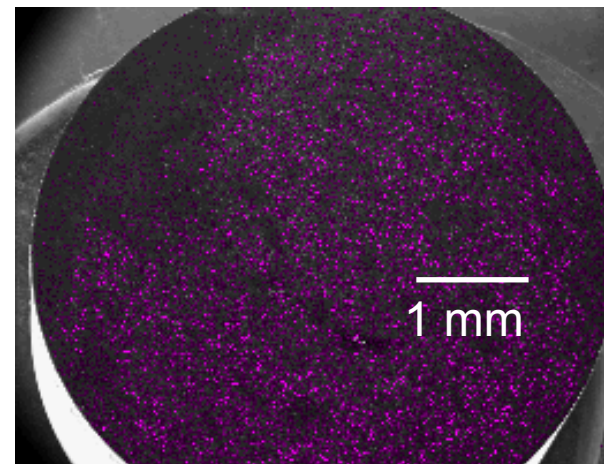
SEM image taken before CVs



Stable CV of Pt/LaB₆ powder in acidic media

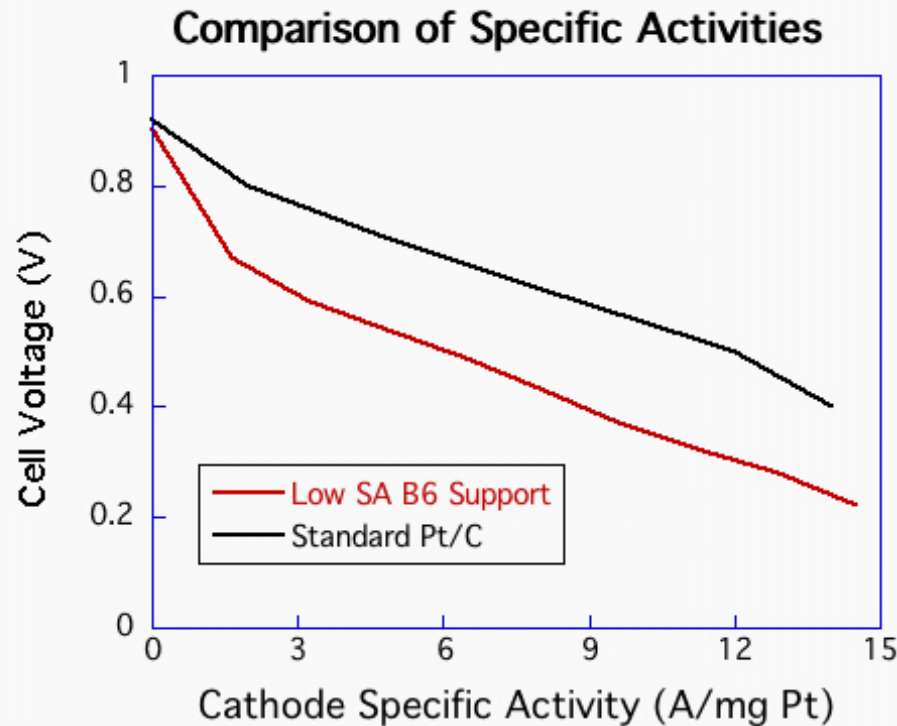


EDAX map showing presence of La after CVs



CV stable after ca. 6th cycle

FC Testing with Pt on low surface area hexaboride

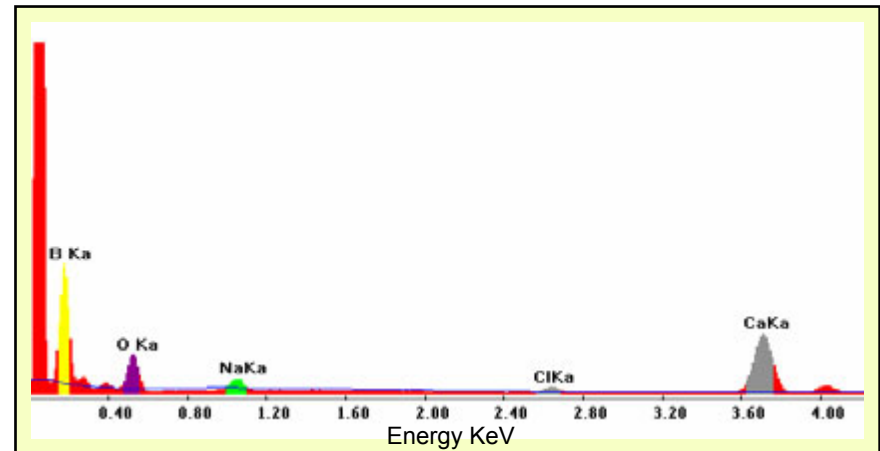
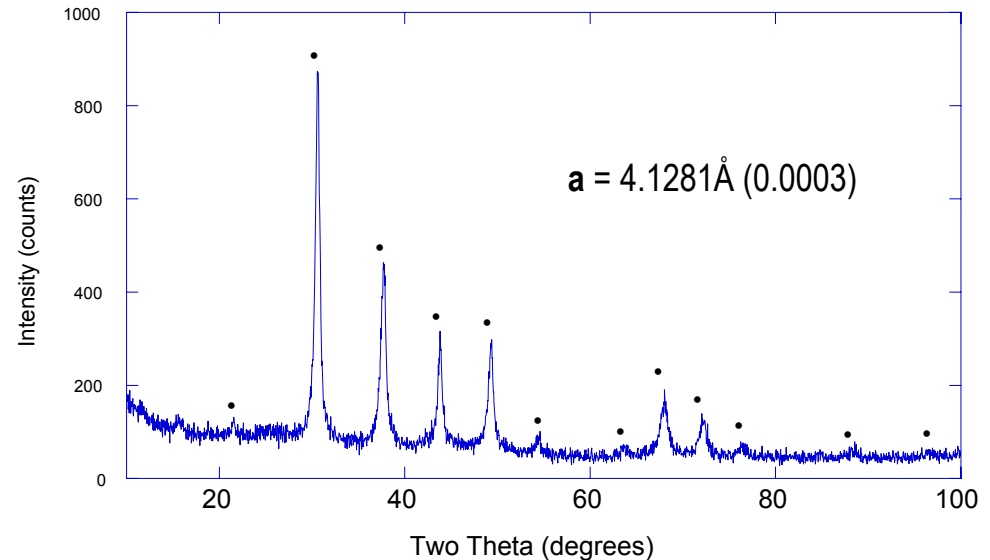


- Low loading of 0.06 mg Pt/cm² on the CeB₆ supported cathode
- Mediocre performance, but:
 - < 1/200th the surface area of the carbon support (in the comparison).
 - Similar catalyst layer thickness - poor transport properties?
- Clearly need high surface area (HSA) hexaborides.

Synthesis of high surface area calcium hexaboride

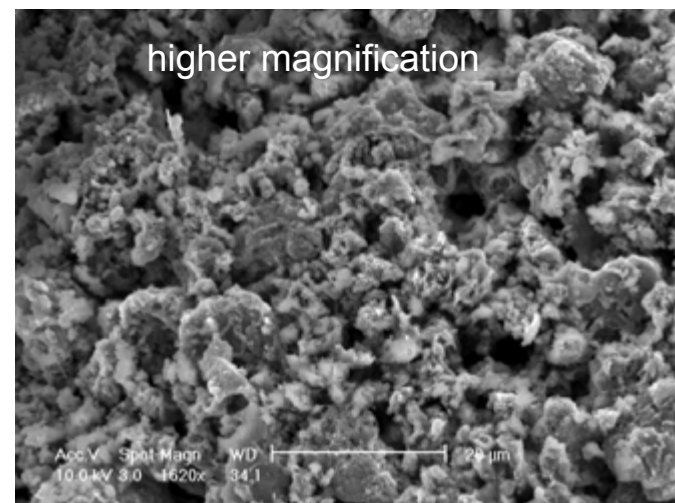
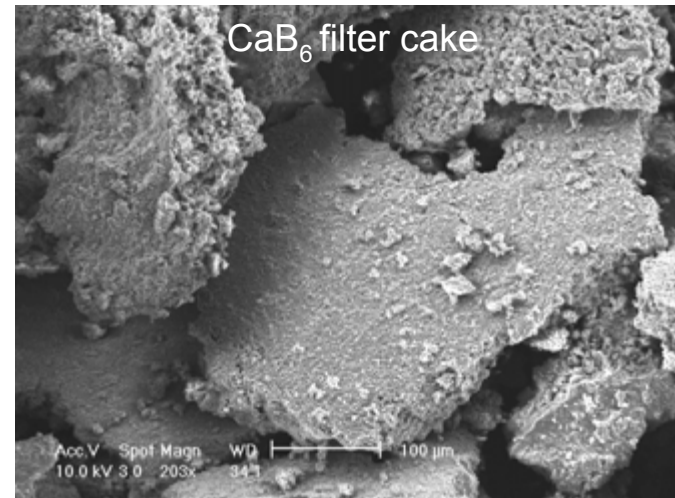
Near single phase CaB_6 obtained through high pressure solid state synthesis.

- Full profile fitting for lattice spacing, particle size and strain yield primitive cubic structure close to literature (4.1535\AA).
- Average XRD-derived columnar size on the order of 295\AA
- EDAX analysis shows predominantly Ca and B with several percent O and traces of Na and Cl left over from precursors.
- O present most likely in form of borate however, XRD indicates it is amorphous.



High surface area calcium hexaboride (cont.)

- SEM analysis indicates rougher surface and higher surface area in general. Occasional fluffy structures attributed to borate.
- Nitrogen BET measurement on this sample gives $240 \text{ m}^2/\text{g}$ - more than 2 orders of magnitude higher than with previous hexaboride synthesis approaches.
- BET surface area > predicted from XRD derived size - suggests appreciable surface roughness.
- Next step - synthesize useful hexaborides.



Future Work

■ Questions and Challenges.

- High Surface Area (HSA) Hexaborides.
 - Synthesis
 - Durability, stability, conductivity and “activity”
- Fuel cell performance.
 - Replicate half-cell performance (temperature effects?).
 - Catalyst layer effectiveness.

■ Remainder of FY'06.

- FC testing of BNL catalysts.
- Expand quantum mechanical models.
 - Include oxidized hexaboride surfaces / link structure and ORR models.
- Further screening of hexaboride materials.
- Continue developing higher surface area (HSA) materials.
 - High pressure/temperature synthesis.
 - Plasma synthesis.
- Continue testing of Pt / hexaborides, particularly HSA materials.
 - CVs, RRDEs, EXAFs etc.
- Fuel cell testing of HSA hexaboride-based catalysts.

Project Summary

■ Relevance and Approach.

- New supports are needed that can sustain activity and integrity of highly dispersed Pt.
- Low work function materials are intriguing candidates.
 - Increase wetting / adhesion of Pt to support (interfacial dipole)
 - Sustain activity of high dispersions (electron donation).
- Hexaborides: low work function supports with promising properties.

■ Technical Accomplishments and Progress.

- Characterized a number of low surface area hexaborides with a variety of techniques. Demonstrated:
 - unusual Pt morphology - not crystallites.
 - activities similar to Pt/C with “subcrystalline” Pt (EuB_6 possibly the best).
 - Pt stable even while support degrades (e.g., CaB_6).
 - support stability difficulties with single crystals.
- Preliminary models of Pt bilayers on LaB_6 , ORR on Pt surfaces.
- Synthesized Ca hexaborides with very high surface areas (untested).

■ Future Research

- Synthesize and test more relevant HSA hexaborides.
 - FC testing with HSA hexaborides.
- Model structures w/ oxides at interface and link with ORR model.

Responses to '05 Reviewers Comments

- “Lack of fundamental criteria for choosing the new support which was not based on previous evaluations of stability, conductivity, and surface area.”
 - In the previous presentation we were unable to go into details due to IP issues, but we are now able to discuss approach. Hopefully, the rationale behind pursuing low work function supports is understandable. Starting from the low work function criteria, we then evaluate the other criteria as there is little or no info in the literature. If instead we first screened for the other criteria, the “solutions” would probably not be any better than carbon regarding “interactivity” with Pt.
- “Need to quickly demonstrate potential CS support under fuel cell conditions.”
 - An understandable point, but poor performance does not necessarily tell us whether it is with the approach or indirect issues (e.g. low surface areas). Until high surface area (HSA) materials are developed, it is desirable to understand the fundamentals as much as possible.
- “Not clear if the solutions developed are applicable for high volume manufacturing.”
 - While there are several papers in the literature on forming HSA hexaborides using vacuum CVD processes (expensive and low throughput), our HSA development efforts have specifically targeted the use of low-cost materials and processes that can be readily scaled up to high throughputs.

FY2006 Publications

Patent application submitted on hexaboride-supported precious metal composite materials and formation thereof.

Critical Assumptions and Issues

- Can suitable High Surface Area (HSA) hexaborides be synthesized?
 - 11th hour results shown with CaB_6 are very promising. Since carbothermal synthesis temperatures, etc., are at least as severe with CaB_6 as with the other hexaborides, it is expected that the more promising hexaborides can be synthesized in HSA form.
- Will HSA Hexaborides have the requisite “activity” and stability?
 - While the large hexaboride particles appear to have sufficient stability (in half-cells, anyway), the concern is that very fine particles may have more significant stability issues. In a similar vein, other properties may be affected. For the most part, it is expected that these quasi-ionic structures will be less susceptible to particle size stability and activity issues than metallic particles.
- Will half-cell performances carry-over to fuel cells?
 - There have been difficulties with us and others in realizing the fuel cell performances predicted by half-cell results. To some extent, these may be catalyst layer transport and utilization issues which may be improved by better catalyst layer design. Other issues, such as the higher temperatures of operating fuel cells, may exacerbate stability problems. If these appear to be issues, we will need to clarify the situation (e.g., run half-cells at the higher temperatures).
- Can significant increases in Pt utilization and longevity be realized?
 - As long as the other issues do not dominate, it is clear that the hexaboride supports offer a beneficial surface compared to carbon and sustain activity even as they corrode away (i.e., the CaB_6). If the support becomes a sacrificial component to maintain high Pt dispersions, their usefulness may come down to whether the hexaborides can stay intact for the desired service life of the stack.