# V.A.3 Electrocatalyst Supports and Electrode Structures

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## Objectives

- Reduce the amount of Pt and platinum group metal (PGM) required.
- Improve Pt catalyst dispersion and durability.
- Improve electrode manufacturability and performance.

## 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:

(A) Durability
(B) Cost
(C) Electrode Performance

## Technical Targets

Insights gained from this project will be applied towards the development of electrode structures that meet the following 2010 Targets for Electrocatalysts for Transportation Applications:

- PGM Total Content – 0.5 g/kW (rated)
- PGM Total Loading – 0.3 mg/cm$^2$ electrode area
- Durability – 5,000 h at ≤80°C with drive cycle
- Mass Activity – 0.44 A/mg Pt at 900 mV (iR-free, 80°C, $O_2$)

## Accomplishments

- Performed computer simulations of a Pt bilayer on hexaboride.
- Characterized nanolayer Pt on hexaborides using XRD, EXAFS, EDX.
- Demonstrated that ORR activity of nanolayer Pt on hexaboride is similar to Pt on carbon (Pt/C).
- RRDE used to demonstrate that nanolayer Pt manifests standard ORR reaction pathway.
- Single-crystal hexaboride studies revealed a dichotomy between powders and crystals.
- Synthesized calcium hexaboride powders significantly smaller than those reported in the literature.

## Introduction

Typical platinum electrocatalysts for acidic media are supported on carbon, even though there is no particular affinity of the Pt for the carbon surface. As a result, platinum nanoparticles supported on carbon easily detach and leave the support [1] or migrate together and coalesce to form larger particles [2], in either case depriving the electrode of active catalyst surface area. Improved utilization and stability of the platinum nanoparticles requires support alternatives to carbon that provide better adhesion or wetting of the catalyst to the support. Also, higher dispersions of Pt are required to meet technical targets. However, below 2 nm, Pt activity plummets [3] possibly due to electronic or structural effects. Thus, supports for high utilization catalysts will also need to be able to sustain the activity of highly dispersed Pt by some manner of promotion or compensation.

## Approach

The general approach is to develop suitable replacements for the Group VIII metal supports shown by Adzic and coworkers at BNL to sustain high Pt activities with near-monolayer dispersions [4,5]. The highly dispersed Pt in these catalysts maintained bulk-like activity because of the near-Pt like environment provided by the underlying support of a fellow Group VIII metal. Otherwise suitable supports that we have tested could not provide an environment that sustained bulk-like Pt activity in very high dispersions. Most likely, the highly dispersed Pt structures were actually electron deficient because of the lack of a bulk

continuum and a lack of any compensation from the support. To donate charge, electropositive (or low work function) materials are needed. In this project, we investigate novel low-work-function supports that promise to satisfy the full array of criteria, as well as offer some unexpected advantages.

Low-work-function supports should also offer advantages in catalyst stability and durability. As discussed above, improved Pt-support adhesion should decrease the mobility of the Pt clusters and hence the particle growth rate by coalescence. Atomistic modeling will also be utilized to help guide the design of effective supports.

## Results

Metal hexaborides, particularly lanthanum hexaboride, are well known for their low work functions and refractory properties. Consequently, they are primarily used as thermionic emitters in electronic microscopes and other electron-emitting devices. Although they can withstand high temperatures and are insoluble in acidic media, there is no indication that they have previously been used in either heterogeneous or electrochemical catalysis. At LANL, the discovery was made that metal hexaborides are able to spontaneously deposit Pt and other noble metals (Au, Pd, Rh, etc.) from solution. About six hexaborides with this property have so far been identified–$LaB_6$, $YB_6$, $CeB_6$, $EuB_6$, $GdB_6$, and $CaB_6$–but most likely all the rare-earth hexaborides share this ability.

The deposition process is very simple. For example, in preparing glassy carbon disk electrodes, the electrode is coated with a film of hexaboride powder from a suspension. Then, a known amount of chloroplatinic acid solution is added to the film using a micropipet. The Pt spontaneously deposits, and the electrode is rinsed to remove the byproducts.

While heavy and visible Pt depositions on hexaboride powders are easily achieved, Pt additions of several weight percent are not readily visible and appear to be highly dispersed. EDX analysis indicated that on such samples Pt is detected in all areas with La and B (i.e., hexaboride). Further, XRD analysis of these several weight percent Pt hexaborides revealed the absence of Pt diffraction peaks. These noncrystalline depositions are then anticipated to be somewhat less than 2 nm in thickness, the approximate resolution threshold of XRD. Lastly, EXAFS of these materials were compared to EXAFS results for carbon supported Pt and Pt-black. While the latter generally shared similar overall features indicative of crystallite clusters, the Pt/hexaboride sample yielded a distinctly different response that may be indicative of a 2-dimensional structure, as opposed to the 3-dimensional structure apparent from the spherical clusters. In short, all the analytical evidence pointed to the formation of a surprisingly uniform nanometer-scale Pt film on the hexaboride support.

Quantum mechanical calculations used to predict the structure of a Pt nanolayer on a $LaB_6$ hexaboride support are shown in Figure 1. Periodic density functional theory calculations in a plane wave basis with ultrasoft pseudopotentials were used to predict the structure of a Pt bilayer. Starting with the idealized initial structure shown in Figure 1(a), the calculations proceed until the lowest energy structure is acquired, shown in Figure 1(b). The resulting structure indicates that the Pt layer is considerably disrupted by the hexaboride substrate. In particular, four Pt atoms have moved into gaps in the $LaB_6$ surface. The disordered nature of the Pt bilayer may contribute to the inability of XRD to detect a crystalline structure. However, the preliminary theoretical calculations require further study to refine the methodology as well as to incorporate oxygen (and possibly OH) into the process and structure.

The activities of the hexaboride-supported Pt nanolayers were investigated using electrochemical techniques. A sample consisting of 4 wt% noncrystalline Pt on a $EuB_6$ powder with a surface area of roughly 1 $m^2/g$ $EuB_6$ provided possibly the best results. This powder was synthesized in-house from europium acetate and high surface area boron carbide at 1,500˚C. A cyclic voltammogram (CV) for the sample is shown in Figure 2. The electrochemically active Pt surface area derived from the area under the hydrogen adsorption features evident in the ca. 0.0–0.4 V range (vs. RHE) is calculated to be 39 $m^2/g$ Pt. While this is not particularly high as far as supported Pt catalysts are concerned, it is exceptional considering that the active Pt surface area is at least as great as surface area of the hexaboride support. As such, this result suggests that the entire support area is covered with Pt (calculated to be ca. 1 nm thick) and that the entire Pt surface is electrochemically active. This coverage and activity in acidic media is unprecedented for a support that is not itself a member of the Group VIII family (Pt monolayers

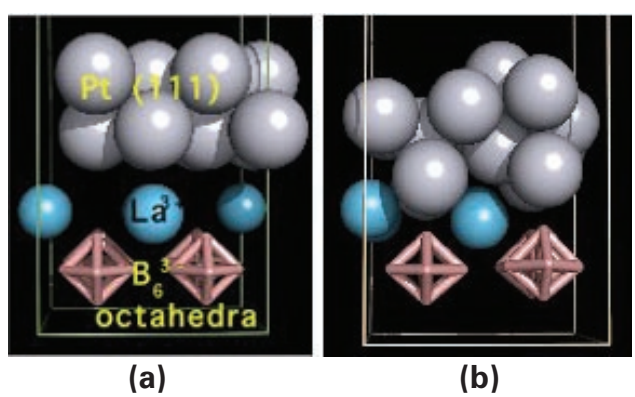


**FIGURE 1.** Computer graphics depicting the starting-point (a) and the subsequent low-energy structure (b) computed for a Pt bilayer on a $LaB_6$ substrate.

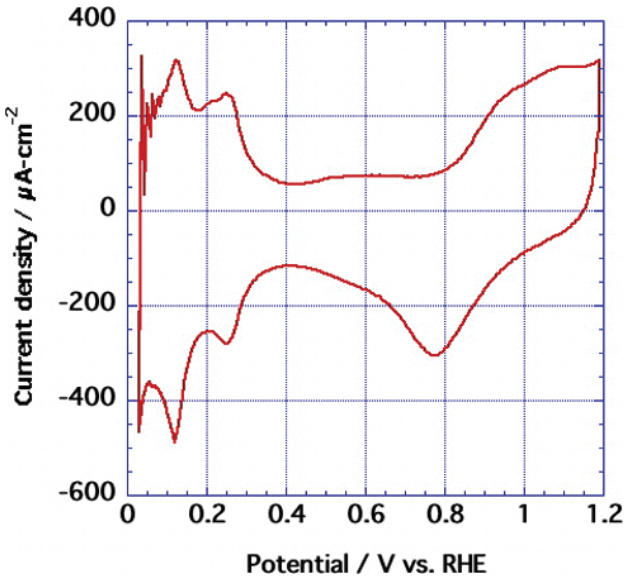


**FIGURE 2.** CV for 4 wt% Pt/$EuB_6$ (Scan rate of 100 mV/s, argon purged 0.5 M $H_2SO_4$)

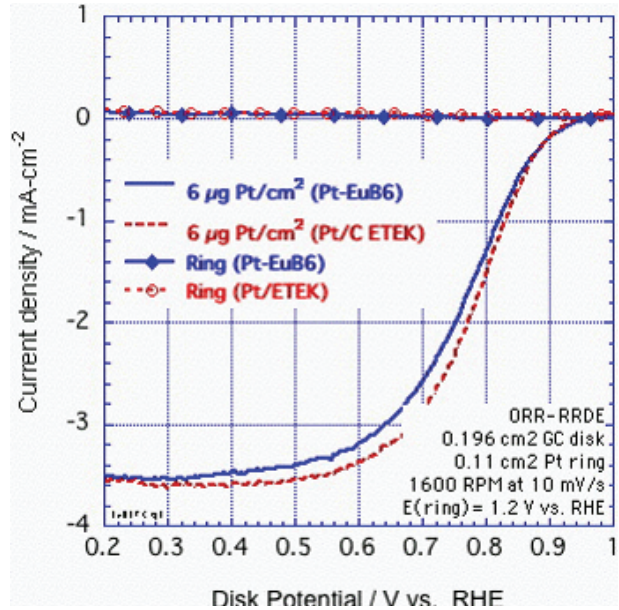


**FIGURE 3.** RRDE Results Comparing the Pt/$EuB_6$ Sample (Figure 2) with Pt/C

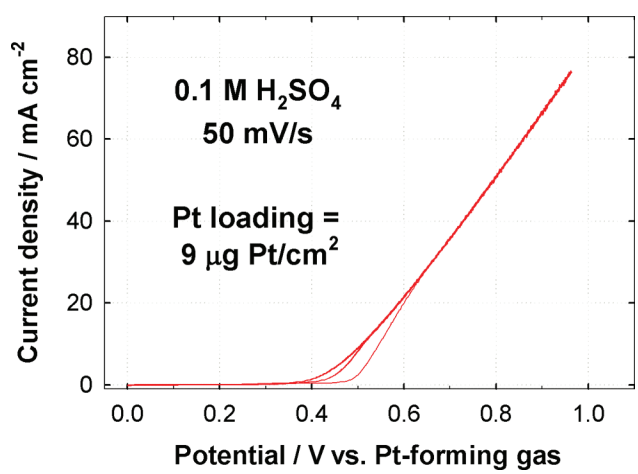


**FIGURE 4.** CVs of Pt/$LaB_6$ (100) in Acidic Media

on Pd and other supports have previously demonstrated high dispersions and activities [4, 5]). Some of the RRDE results for this sample are shown in Figure 3 in comparison to a commercial Pt/C catalyst. Despite the surface area differences of roughly 39 vs. 100 $m^2$/g Pt, the hexaboride support results are quite similar to the Pt/C results, particularly at the onset of ORR. Likewise, the ring results are identical, suggesting that the ORR reaction pathways are the same for the two catalysts. In short, not only does the Pt show unusual affinity and adhesion to the hexaboride support to remain in a highly dispersed configuration, but the electrochemical results suggest that the hexaboride also manages to sustain the activity of the highly dispersed Pt nanolayer. A possibility is that the significant electron transfer from support to catalyst caused by the considerable work function difference results in a strong dipole at the interface. The strong dipole may improve adhesion and wetting of the catalyst to the support and the charge transfer may compensate for electron deficiencies in the noncrystalline Pt. Because of these effects, the expectation is that the catalyst is more firmly anchored to the support (than on carbon) and not as likely to detach or to coalesce into larger particles during operation.

In an effort to more fully characterize the Pt/hexaboride interface, single crystals of $LaB_6$ were investigated. The CV for a (100) crystal face coated with a Pt nanolayer is shown in Figure 4. As can be seen, 0.4 V is the onset of a large ohmic oxidation current. The effects are readily evident in the post-CV SEM shown in Figure 5, where the originally smooth (100) crystal face has become severely pitted during the CVs. While several large initial oxidation sweeps are obtained with Pt-deposited powders, the CVs quickly stabilize (e.g., like the one shown in Figure 2). It was consequently surprising that the crystal faces (several were tested) continued decomposing unabated. To test the susceptibility of the single crystal material, it was crushed into a powder and tested in the manner as the previous powders. The results are shown in Figure 6. Much as with the previous powders, several large oxidation features are obtained with the initial cycles (top graph), which quickly settle into a stable CV (lower graph). Thus, the vulnerability of the single crystals was not a material related issue, but a geometric aspect. A partial explanation for the dichotomy is that the hexaboride materials are not stable until fully encapsulated by the deposition, and the planar surfaces

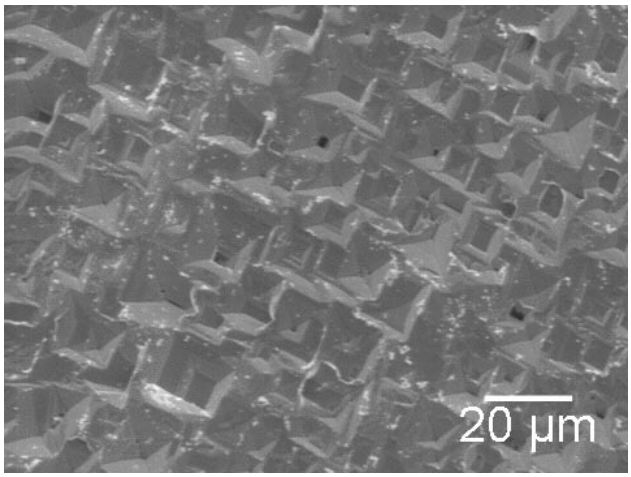


**FIGURE 5.** SEM Image of $LaB_6$ (100) Surface after CVs

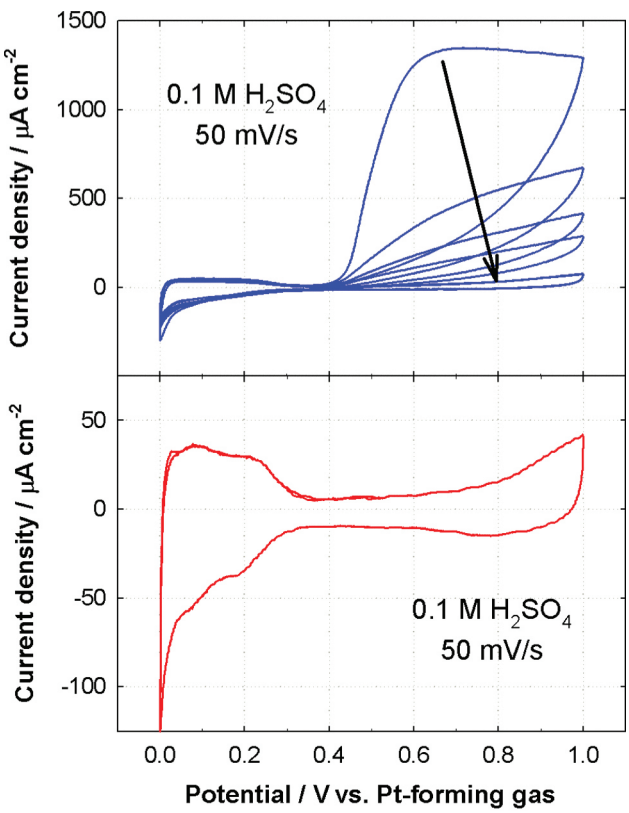


**FIGURE 6.** CVs of Crushed Single Crystal $LaB_6$ Powder (top: initial cycles, lower: stable CV)

are more difficult to protect than the powders. As pits are etched into the hexaboride single-crystal faces, the surface area increases (rather than decreases, as in the case of the powders). As a result, the susceptible hexaboride area grows ahead of its protection as well as possibly undermines previously intact nanolayers.

## Conclusions and Future Directions

In summary, hexaboride supports appear to offer unusual properties for attaining and stabilizing Pt nanolayers and promoting electrochemical activity even with noncrystalline structures. These properties are most likely due to the unusually low work functions of hexaborides. The hexaboride supports are promising for attaining highly dispersed Pt catalysts that are sufficiently stable and active for transportation applications. Further work in characterizing the Pt-hexaboride system is required and meaningful materials for fuel cells need to be developed and tested. Particularly, much higher hexaboride surface areas are necessary. Traditionally, hexaborides are synthesized at about 1500°C, which inadvertently leads to large particles and low surface areas. Using a lower temperature synthesis process, we recently synthesized a roughly 240 $m^2/g$ $CaB_6$, but the process needs improvement and must be replicated with more desirable hexaborides. Further work will be pursued with these relatively inexpensive bulk synthesis processes.

Another intriguing approach to decrease hexaboride particle sizes is microwave frequency plasma torch synthesis. In this method (a recently added capability at LANL), a microwave plasma torch generates temperatures up to 3,000K in less than a microsecond. The highly reducing atmosphere combined with high reaction temperatures and the short reaction times may enable the synthesis of hexaborides with desirable particle sizes and surface areas.

## Special Recognitions & Awards/Patents Issued

**1.** F. A. Uribe, M. S. Wilson, F. H. Garzon, "Composite Materials and Method of Making," Patent Pending.

## FY 2006 Publications/Presentations

**1.** A presentation regarding the overall project status was given at the DOE Annual Merit Review Meeting (May 2006).

## References

**1.** J. Xie, D. L. Wood, K. L. Moore, P. Atanassov, R. L. Borup, *J. Electrochem. Soc.*, **152**, A1011 (2005).

**2.** M. S. Wilson, F. H. Garzon, K. E. Sickafus, S. Gottesfeld, *J. Electrochem.Soc.,* **140,** 2872 (1993).

**3.** K. Kinoshita, *J. Electrochem.Soc.,* **137**, 845 (1990).

**4.** K. Sasaki, Y. Mo, J. X. Wang, M. Balasubramanian, F. Uribe, J. McBreen, R. R. Adzic, *Electrochim. Acta*, **48**, 3841 (2003).

**5.** K. Sasaki, J. X. Wang, M. Balasubramanian, J. McBreen, F. Uribe, R. R. Adzic, *Electrochim. Acta*, **49**, 3873 (2004).