

## V.L.3 Metallic Bipolar Plates with Composite Coatings

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### Objectives

Develop a fluoropolymer-inorganic filler composite coating that is electrically conductive and provides a physical barrier to corrosive species within the fuel cell.

- Apply the composite coating to aluminum alloy substrates using an established high-volume manufacturing process.
- Synthesize titanium diboride ( $\text{TiB}_2$ ) and calcium hexaboride ( $\text{CaB}_6$ ) powders using a low-cost process.
- Measure the  $\text{H}_2$  permeation flux, corrosion resistance, and area specific resistance of the composite coated aluminum plates.
- Demonstrate the ability to make the surface of the coatings hydrophilic.
- Create a flow field design for a plate with an active area  $>50 \text{ cm}^2$ , make stamping dies for the design, and demonstrate the ability to stamp aluminum sheets.

### Technical Barriers

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

(A) Durability

(B) Cost

(D) Water Transport within the Stack

### Technical Targets

The goal of this work is to develop an aluminum-based bipolar plate that meets all of the DOE technical targets for bipolar plates shown in Table 1 [1]. This goal will be met by applying a composite coating that is both electrically conductive and corrosion-resistant to the aluminum plate using an established high-volume manufacturing process.

**TABLE 1.** Project Progress toward Meeting DOE Technical Targets for Bipolar Plates [1]

Characteristic	Units	2015 Target	Project 2010 Status
Cost	\$/kW	3	TBD
Weight	kg/kW	<0.4	TBD
$\text{H}_2$ Permeation Flux	$\text{cm}^3 \text{ sec}^{-1} \text{ cm}^{-2}$ @ 80°C, 3 atm	<2 x 10 <sup>6</sup>	<2 x 10 <sup>6</sup>
Corrosion	$\mu\text{A}/\text{cm}^2$	<1	<1
Electrical Conductivity	S/cm	>100	33
Resistivity	Ohm-cm	0.01	0.03
Flexural Strength	MPa	>25	TBD
Flexibility	% deflection at midspan	3 to 5	TBD

TBD: To be determined

### Accomplishments

- $\text{TiB}_2$  and  $\text{CaB}_6$  powders have been synthesized using a low-cost process that is scalable. An invention disclosure is being filed for the  $\text{CaB}_6$  synthesis procedure.
- High aspect ratio metal boride powder synthesis has been demonstrated.
- The stability of  $\text{TiB}_2$  and  $\text{CaB}_6$  has been tested at 80°C in sulfuric acid solutions.
- Composite coatings have been applied to aluminum substrates using electrostatic spraying and wet spraying; both are high volume manufacturing processes.
- Corrosion resistance that exceeds the DOE targets has been measured for composite-coated aluminum plates under both anodic and cathodic conditions for 24 hours.
- Hydrophilic coating surface properties were achieved using a simple two-step process.

- A flow field design and the corresponding stamping dies were created and used to stamp 75 pieces of aluminum alloy.
- The H<sub>2</sub> permeation flux of the stamped aluminum plates was measured under the conditions specified in the DOE target and no hydrogen permeation was detected.
- Baseline single cell tests were performed on the uncoated, stamped aluminum bipolar plates for 300 hours.



## Introduction

Aluminum bipolar plates offer a potential weight reduction of up to 65% over stainless steel, while still having the desired mechanical properties that a metal offers. Furthermore, untreated aluminum can meet all of the DOE bipolar plate targets except for corrosion resistance. To overcome this one weakness, we have been applying a composite coating consisting of a matrix of an acid-resistant fluoropolymer and a filler material that is electrically conductive and acid-resistant. Metal borides and carbon-based materials, such as graphite, carbon black, and carbon fibers, were identified as candidate filler materials. Composite-coated aluminum bipolar plates can be fabricated using techniques, such as stamping, welding, and spraying, that are currently used for high-volume manufacturing of many consumer goods. In the first year of the project, we have focused on the H<sub>2</sub> permeation, corrosion, and electrical properties targets.

## Approach

In order to meet the cost target using metal boride filler materials, it was necessary to develop a low-cost metal boride synthesis process. Furthermore, the use of high aspect ratio filler powders would allow for a reduction in the volume fraction of the filler (for lower costs), so synthesis procedures to obtain such filler powders were also developed. We have worked on identifying the combination of fluoropolymer and filler that will provide the desired electrical conductivity in a composite coating. We have made free-standing composite films and sprayed fluoropolymer (ethylene-tetrafluoroethylene, ETFE or polychlorotrifluoroethylene, PCTFE) mixed with either graphite or carbon fibers onto non-conductive substrates, and we have measured the surface conductivity/resistivity of these samples. We have varied the type of graphite, the type of fluoropolymer, and the ratio of filler to fluoropolymer in an effort to increase the electrical conductivity of the coatings. Other subtasks include corrosion testing of coated aluminum panels, flow field design and stamping of aluminum plates, and

hydrogen permeation measurements. We have also developed a treatment procedure for making the coating surface hydrophilic to ease water transport within the stack.

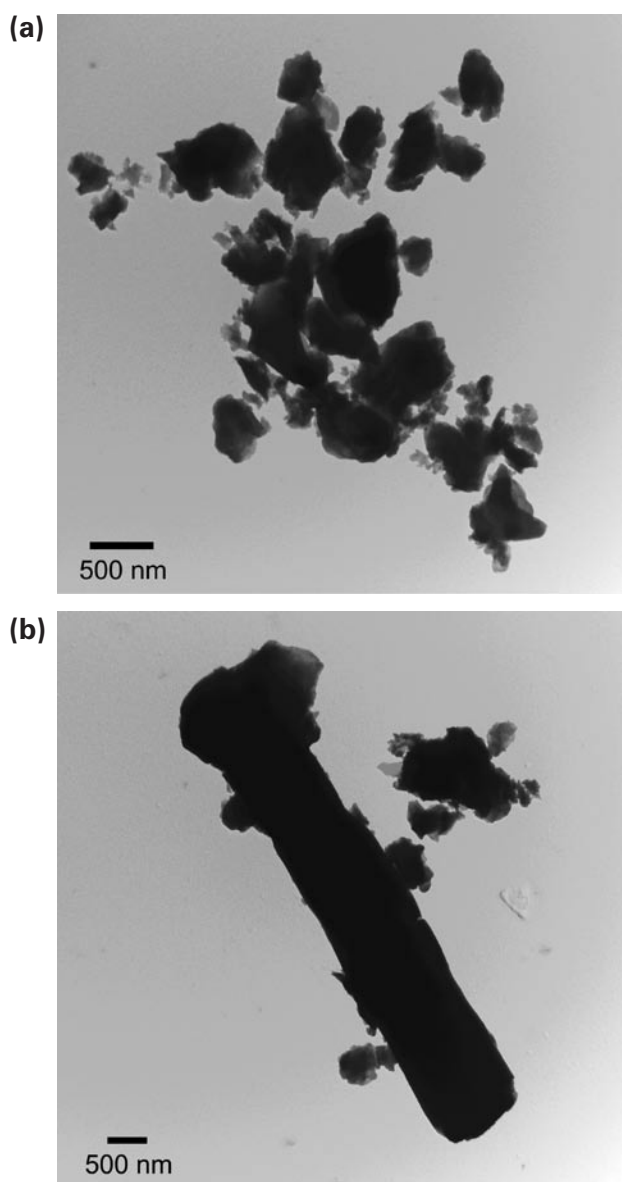
## Results

Of the metal borides, TiB<sub>2</sub> and CaB<sub>6</sub> were chosen because they have the desired combination of reported electrical conductivity [2], density, and corrosion resistance [3]. Low-cost processes were developed and used to synthesize TiB<sub>2</sub> [4] and CaB<sub>6</sub>. Inexpensive Ti, Ca, and B precursors were used in the 3-step synthesis procedures, which used processing temperatures of up to 1,600°C. Powder X-ray diffraction (XRD) results showed only the desired metal boride product and, in the case of TiB<sub>2</sub>, a small amount of excess carbon. Analysis by transmission electron microscopy (TEM) showed that particle sizes were, on average, sub-micrometer in diameter, Figure 1a. By adding a small amount of a seed element, elongated grains could be grown, Figure 1b.

It is reported that the environment inside a proton exchange membrane (PEM) fuel cell is acidic due to the presence of the Nafion<sup>®</sup> membrane and Nafion<sup>®</sup> ionomer in the electrodes combined with the humidity [5]. Acid stability tests were conducted on commercially purchased and SIUC-synthesized TiB<sub>2</sub> and CaB<sub>6</sub> at 80°C under 3.5% H<sub>2</sub> in helium with reflux. Two sulfuric acid solutions were used in the tests: 1) 0.5 M H<sub>2</sub>SO<sub>4</sub> (pH=1) with 2 ppm NaF and 2) 0.001 M H<sub>2</sub>SO<sub>4</sub> (pH=3) with 0.1 ppm NaF. The results of the tests are shown in Table 2. The values shown in the “% Sample Remaining” column were calculated from the measured change in weight of the samples. Neither of the borides was found to be completely resistant to the acid, but CaB<sub>6</sub> performed better than TiB<sub>2</sub>.

Electrochemical corrosion experiments were also conducted on the CaB<sub>6</sub> and TiB<sub>2</sub> powders to corroborate the findings of the acid stability tests. Powders of TiB<sub>2</sub> (Cerac, -200 mesh) and CaB<sub>6</sub> (Alfa Aesar, -325 mesh) were ball-milled in ethanol and then mixed with Nafion<sup>®</sup>. A thin film of the mixture was applied to a rotating disk electrode and electrochemically tested in both O<sub>2</sub>-saturated and O<sub>2</sub>-free (i.e., Ar purged) 0.1 M H<sub>2</sub>SO<sub>4</sub>. Potential holds at several potentials and potential scans that are relevant to the bipolar plate application were run. The measured corrosion currents were higher than the DOE target of 1 x 10<sup>-6</sup> A/cm<sup>2</sup>, indicating that both CaB<sub>6</sub> and TiB<sub>2</sub> would not be stable in the PEM fuel cell environment.

Surface electrical conductivity/resistivity measurements of free-standing composite samples were measured using a four-point probe (Jandel) driven by a potentiostat. The free-standing samples were made by mixing the appropriate amounts of PCTFE and the



**FIGURE 1.** TEM Images of  $\text{CaB}_6$  Synthesized by a Low-Cost Process: (a) Original Process, (b) Modified Process to Produce Elongated Grains

desired filler powders, and then uniaxially pressing them at  $235^\circ\text{C}$  to sinter the fluoropolymer and form a solid disk. Selected conductivity results are shown in Table 3 for samples that had 60 vol% electrically conductive filler with 40 vol% PCTFE. The measured electrical conductivities of the composites were significantly lower than the published bulk conductivities of the fillers. This is likely due to contact resistance between the filler particles. Furthermore, the PCFTE may act to separate the filler particles as it flows between the particles during sintering. Also, in the case of  $\text{CaB}_6$ , it is suspected that the published bulk value is erroneously high [6,7].

Based on the results in Table 3 and the acid stability tests showing that the borides are unstable, we

**TABLE 2.** Results of the Sulfuric Acid Stability Experiments at  $80^\circ\text{C}$  in 3.5% Hydrogen

Sample	pH	Time (days)	% Sample Remaining	Extra Phases in XRD
$\text{TiB}_2$ (Cerac, -200 mesh)	1	8	<1	n.a.
$\text{TiB}_2$ (Cerac, -200 mesh)	3	20	77	$\text{TiO}_2$
$\text{TiB}_2$ (SIU)	3	27	95	$\text{TiO}_2$ , $\text{H}_3\text{BO}_3$ , $\text{TiOSO}_4$
$\text{CaB}_6$ (Alfa Aesar, -325 mesh)	1	8	131	$\text{H}_3\text{BO}_3$
$\text{CaB}_6$ (Aldrich, -200 mesh)	3	15	67	none
$\text{CaB}_6$ (SIU)	3	31	92	none

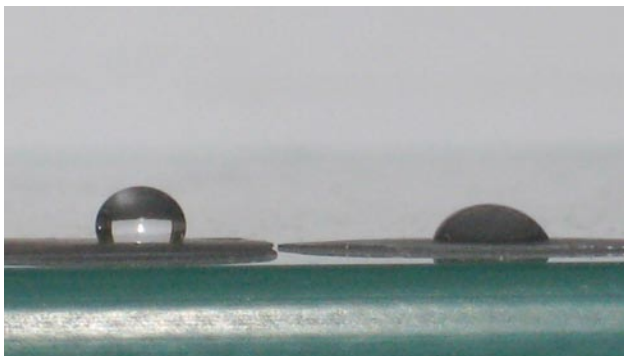
n.a. = not analyzed

**TABLE 3.** Selected Results of 4-Point Electrical Conductivity Measurements on Free-Standing Composite Samples (60 vol% filler/40 vol% PCTFE)

Filler	Published Bulk Conductivity (S/cm)	Measured Conductivity of Composite (S/cm)	Supplier
Carbon Black	0.1-100 [8]	$5.0 (\pm 0.2)$	Cabot
Graphite (spheroidized)	333-2,000 [9]	$4.4 (\pm 1.0)$	Superior Graphite
Graphite (flake)	333-2,000 [9]	$26.3 (\pm 1.9)$	Alfa Aesar
$\text{CaB}_6$	4,500 [2]	$0.57 (\pm 0.15)$	Aldrich
$\text{TiB}_2$	111,000 [2]	$11.2 (\pm 1.6)$	Cerac

proceeded to investigate composite coatings that had graphite-based fillers. Slurries were made by ball milling the desired amounts of graphite and fluoropolymer with solvents. They were then sprayed onto a non-conductive ceramic substrates and the resistivity/conductivity was measured using the 4-point probe. A composition that was 40% flake graphite, 20% spheroidized graphite, and 40% EFTE was found to have the best resistivity of  $0.03 \Omega\text{-cm}$ .

Having a hydrophilic surface on the bipolar plate aids with water management in the electrodes, so we have invented a method for changing the PCFTE surface from hydrophobic to hydrophilic by applying two solutions, sequentially, and heating the film up to  $135\text{-}150^\circ\text{C}$  for 5 minutes after each application. This method was demonstrated on a 60% graphite-filled PCTFE film, as shown in Figure 2, and on similar coatings that were sprayed onto aluminum. Contact angle measurements made using a First Ten Ångströms system yielded contact angles of  $108^\circ$  for the untreated sample (Figure 2, left) and  $65^\circ$  for the treated sample (Figure 2, right).



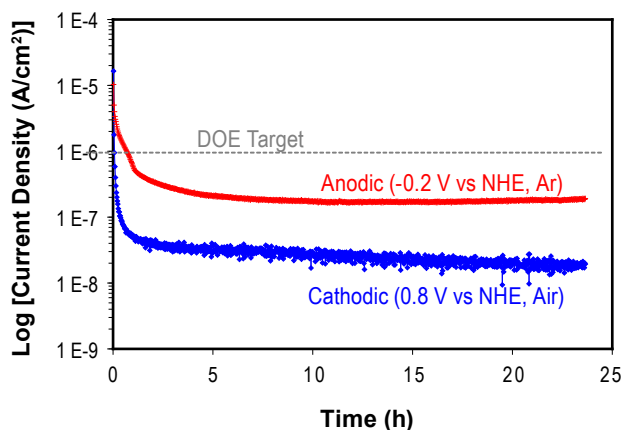
**FIGURE 2.** Water Droplets on Untreated (left) and Treated (right) Graphite-PCTFE Composites

Corrosion resistance measurements of coated aluminum samples using electrochemical methods [10] were conducted to evaluate the ability of the coatings to provide a physical barrier between the aluminum substrate and the corrosive media in a fuel cell. In these experiments, the electrolyte was 0.001 M sulfuric acid ( $\text{pH} = 3$ ) with 0.1 ppm NaF. For cathodic corrosion tests, air was bubbled continuously through the acid solution and 0.6 V vs. Ag/AgCl (or 0.8 V vs. normal hydrogen electrode, NHE) was applied for 24 hours. For anodic corrosion tests, argon was continuously bubbled through the acid solution and -0.4 V vs. Ag/AgCl (or -0.2 V vs. NHE) was applied for 24 hours. The results for aluminum plates with a coating of 20 vol% carbon fiber/80 vol% EFTE applied by electrostatic spraying at Orion Industries are shown in Figure 3. The current densities fall below the DOE corrosion target, showing that the coatings provide a stable barrier.

A total of 75 uncoated aluminum bipolar plates with flow fields have been stamped with a  $60 \text{ cm}^2$  active area. The design is based on a GTI patented trapezoid flow field structure for PEM fuel cells with very low pressure drop. The hydrogen permeability of the formed plates was tested and there was no hydrogen pass-through detected at 50 psig (3.4 atm), meeting the DOE target. In addition, the bipolar plate design was proven during fuel cell testing which demonstrated that the stacks can be well sealed against fuel, oxidant, and cooling water leaks. During fuel cell lifetime testing using the bare, uncoated aluminum bipolar plates, it was found that the use of aluminum leads to high electrical resistance, which increases with time. These baseline data will be used for comparison against the coated aluminum plates.

### Conclusions and Future Directions

- $\text{TiB}_2$  and  $\text{CaB}_6$  are not sufficiently acid resistant for use in PEM fuel cell stacks.
- Composites made with flake graphite as the filler have the highest electrical conductivities.



**FIGURE 3.** Corrosion Resistance Measurements for Carbon Fiber-PCFTE Coated Aluminum Panels

- Composite coatings on aluminum meet the DOE technical target for corrosion resistance.
- Aluminum blocks hydrogen permeation and meets the DOE technical target for hydrogen permeation.
- The surfaces of our coatings can be treated to make them hydrophilic.
- In future work, we will continue to explore methods and new coating compositions for increasing the electrical conductivity and reducing the resistivity. Contact resistance and area specific resistance measurements will also be conducted.
- The stamped and welded aluminum bipolar plates ( $>50 \text{ cm}^2$ ) will be sent to Orion Industries for coating application and then sent to GTI for single cell testing.
- A cost analysis will be conducted.

### Special Recognitions & Awards/Patents Issued

1. J.D. Carter, J.R. Mawdsley, S.G. Niyogi, T.A. Cruse, X. Wang, and L. Santos, "Corrosion Resistant Bipolar Plate for Polymer Electrolyte Fuel Cells", U.S. Patent No. 7699916, April 20, 2010.

### References

1. "Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan", U.S. Department of Energy, Hydrogen, Fuel Cells & Infrastructure Technology Program, DOE/GO-102007-2430, 2007.
2. G.V. Samsonov and I.M. Vinitkii, *Handbook of Refractory Compounds*, IFI/Plenum, New York, NY (1980).
3. N.N. Greenwood, R.V. Parish, and P. Thorton, "Some Reactions of Metal Borides," *J. Chem. Soc.* (1965) 545-549.

4. R. Koc and D.B. Hodge, "Production of  $TiB_2$  from a precursor containing carbon coated  $TiO_2$  and  $B_4C$ ," *Journal of Materials Science Letters*, **19** (2000) 667-669.
5. D. Knigge, T. Jacksier, E. Claude, and A. Milahi-SC. "Electrochemical Corrosion Testing and In-Stack Aging of Metallic Bipolar Plates for PEM Fuel Cells" in *Proceedings of the 16th World Hydrogen Energy Conference*, 2006.
6. S. Souma, H. Komatsu, T. Takahashi, R. Kaji, T. Sasaki, Y. Yokoo, and J. Akimitsu, "Electronic Band Structure and Fermi Surface of  $CaB_6$  Studied by Angle-Resolved Photoemission Spectroscopy," *Phys. Rev. Lett. (USA)*, **90** [2] (2003).
7. H.J. Tromp, P. van Gelderen, P.J. Kelly, G. Brocks, and P.A. Bobbert, " $CaB_6$ : A New Semiconducting Material for Spin Electronics," *Phys. Rev. Lett. (USA)*, **87** [1] (2001) 016401/1-016401/4.
8. D. Pantea, H. Darmstadt, S. Kaliaguine, L. Summchen, and C. Roy, "Electrical conductivity of thermal carbon blacks - Influence of surface chemistry," *Carbon*, **39** [8] (2001) 1147-1158.
9. P.D. Ownby and R.W. Stewart, "Engineering Properties of Diamond and Graphite" in *Ceramics and Glasses S.J. Schneider*, Editor, ASM International, p. 821-834, 1991.
10. H.L. Wang, M.A. Sweikart, and J.A. Turner, "Stainless steel as bipolar plate material for polymer electrolyte membrane fuel cells," *Journal of Power Sources*, **115** [2] (2003) 243-251.