V.H.2 Metallic Bipolar Plates with Composite Coatings

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Fiscal Year (FY) 2011 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.
- Measure the corrosion resistance at 80°C and area specific resistance of the composite coated aluminum plates.
- Apply the composite coating to stamped and welded bipolar plates, and then conduct a single cell, 2,000-hour test.
- Conduct an analysis to determine the anticipated cost of manufacturing the plates at high volume.

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
(C) Performance

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. 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 2011 Status
Cost	$/kW	3	TBD
Weight	kg/kW	<0.4	0.35
H_2 Permeation Flux	$cm^3\ sec^{-1}\ cm^{-2}$ @ 80°C, 3 atm	$<2 \times 10^6$	$<2 \times 10^6$
Corrosion	$\mu A/cm^2$	<1	<1 (cathodic) 11 (anodic)
Electrical Conductivity	S/cm	>100	37
Area Specific Resistance[a]	$Ohm\text{-}cm^2$	0.02	0.58
Flexural Strength	MPa	>25	TBD
Flexibility	% deflection at midspan	3 to 5	TBD

[a] Tentative revised target
TBD – to be determined

FY 2011 Accomplishments

- Nano-size titanium carbide (TiC) powder has been synthesized using a low-cost process that is scalable.
- A patent application has been filed for the low-cost CaB_6 powder synthesis procedure.
- TiC was identified as the most acid resistant of the cermet powders tested for acid stability and electrochemical stability at 80°C and room temperature in sulfuric acid solutions.
- Substituting nano-size TiC for half of the flake graphite filler in the composite coatings was found to significantly reduce area specific resistances of the coated aluminum samples.
- The composite coated aluminum plates meet the DOE target for electrochemical corrosion resistance under cathodic conditions at 80°C.
- Composite-coated, stamped aluminum plates were made using wet spraying, a high volume manufacturing process.

- A composite-coated, stamped aluminum plate tested in a single-membrane electrode assembly (MEA), two-bipolar plate cell test showed improved performance over untreated aluminum.

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Introduction

Aluminum bipolar plates offer a potential weight reduction 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, the project team has 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 carbides, metal borides, metal silicides, and carbon-based materials, such as graphite, carbon black, and carbon fibers, were identified as candidate filler materials based on reported electrical conductivity and acid resistance properties [2]. In the first year of the project, we found that metal borides were not stable under simulated fuel cell conditions, so in the second year, TiC and titanium disilicide ($TiSi_2$) were evaluated. The composite-coated aluminum bipolar plates have been being fabricated using techniques, such as stamping, welding, and spraying, that are currently used for high-volume manufacturing of many consumer goods. In the second year of the project, we have focused on meeting the corrosion and electrical properties targets.

Approach

The titanium carbide powder currently available commercially is expensive and not available in sub-micrometer sizes. So, titanium carbide was made at Southern Illinois University (SIU) using a low-cost process that produces nano-size particles [3]. Acid stability tests at 80°C and electrochemical stability tests in sulfuric acid were conducted to determine if TiC and $TiSi_2$ are durable enough for use in proton exchange membrane (PEM) fuel cells. Argonne has worked on identifying the formulation of fluoropolymer and filler that can provide the desired electrical conductivity in a composite coating. We have sprayed fluoropolymer (ethylene-tetrafluoroethylene, EFTE, or polychlorotrifluoroethylene, PCTFE) mixed with TiC, graphite, and/or carbon black onto non-conductive substrates, and we have measured the surface conductivity/resistivity of these samples. We have varied the ratio of graphite to TiC, the type of fluoropolymer, and the ratio of filler to fluoropolymer to increase the electrical conductivity of the coatings. We have conducted electrochemical corrosion studies of the coated aluminum samples at 80°C using the conditions specified by the DOE. Finally, initial tests were conducted of stamped, welded, and coated aluminum plates in a single cell test.

Results

Of the metal carbides, TiC was chosen because it has the desired combination of reported electrical conductivity, density, and corrosion resistance [2]. Low-cost processes were used to synthesize nano-size TiC powder at SIU. These processes allowed for tuning the electrical properties of the powder. Inexpensive TiO_2 and propylene precursors were used in the 2-step synthesis procedure, which used processing temperatures of up to 1,500°C. Powder X-ray diffraction results showed only the desired titanium carbide phase. Analysis by scanning electron microscope (SEM) showed that particle sizes were, on average, <200 nm in diameter, Figure 1, and that the particles formed an interconnected network.

The environment inside a PEM fuel cell is acidic due to the presence of the Nafion® membrane and the Nafion® ionomer in the electrodes, combined with the humidity [4]. Acid stability tests were conducted on the synthesized TiC, graphite (Superior Graphite), and $TiSi_2$ at 80°C in 3.5% H_2 in helium for 30 days. The sulfuric acid solution used in the tests was 0.001M H_2SO_4 (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 the weight of the samples.

Electrochemical corrosion experiments using the thin-film rotating disk-electrode technique were also conducted on the TiC and $TiSi_2$ powders to corroborate the findings of the acid stability tests. Powders of TiC (SIU) and $TiSi_2$ (Aldrich, ball milled) were made into an ink by mixing them

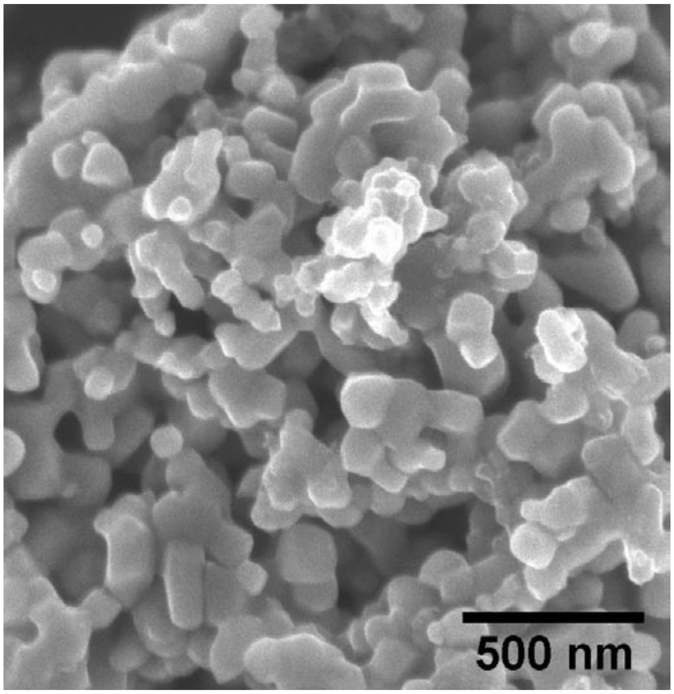

FIGURE 1. SEM Images of Nano-Size TiC Powder Synthesized by a Low-Cost Process at SIU

TABLE 2. Results of the Sulfuric Acid Stability Experiments at 80°C in 3.5% Hydrogen

Sample	% Sample Remaining	Extra Phases in XRD	Ion Concen. (mol/L)
TiC	109%	none	Ti: n.d.*
$TiSi_2$ (with TiSi & Si impurities)	132%	Ti_3O_5, TiO_2	Ti: n.d.* Si: $5.6x10^{-3}$
Graphite	94 %	none	n.a.

*The detection limit is $1.3x10^{-6}$ mol Ti/L
n.a. – not analyzed; n.d. – not determined

with Nafion® and an organic solvent. The volume ratio of the powder to dry Nafion® was 50:50. A thin film of the mixture was applied to a rotating disk electrode (RDE) and electrochemically tested at room temperature in both O_2-saturated and O_2-free (Ar-purged) 0.1 M H_2SO_4. The loading of powder on the RDE was 155 μg/cm^2. Potential holds at several potentials and potential scans relevant to the bipolar plate application were run. The results are shown in Table 3. The $TiSi_2$ sample performed the best with no redox features observed in the cyclic voltammetry (CV) tests. The TiC was acceptable, but a small oxidation peak at 0.56 V occurred when cathodic scan went to a potential less than 0.4 V. Since these tests were performed at room temperature there are some differences from the acid stability experiments. Based the results from the two types of stability tests, TiC was chosen as the best candidate, along with graphite and carbon black, for the filler phase in the composite coatings.

TABLE 3. Results of RDE Electrochemical Stability Experiments

Sample	Corrosion Current (A/cm^2)			Observations
	0.84 V in Ar	0.84 V in O_2	0.14 V in Ar	
TiC (SIU)	6.24×10^{-6}	1.34×10^{-5}	7.06×10^{-6}	A small oxidation peak at 0.56 V occurred when cathodic scan went to a potential less than 0.4 V.
TiC (Aldrich, milled)	4.92×10^{-5}	2.87×10^{-5}	2.27×10^{-5}	Same features as for unmilled SIU TiC
$TiSi_2$ (Aldrich, milled)	5.65×10^{-6}	5.70×10^{-6}	4.75×10^{-6}	No obvious redox features

Surface electrical conductivity/sheet resistance were measured using the Van der Pauw technique [5] and a four-point probe (Jandel) on the composite coatings deposited on non-conductive ceramic substrates. Through-sample area specific resistivity (ASR) measurements [6,7] were conducted at an applied pressure of 200 psi on aluminum-based samples that were coated on both sides. Slurries were made by ball milling the desired amounts of filler (graphite, nano-size TiC, and/or carbon black) and fluoropolymer (PCTFE or ETFE) with solvents. The slurries were then sprayed onto either aluminum or ceramic substrates and sintered at 240 to 300°C for 2 to 4 h. Selected ASR and sheet resistance results are shown in Table 4. The measured electrical conductivities of the composites were significantly lower than the published bulk conductivities of the fillers possibly because the fluoropolymer may act to separate the filler particles as it flows between the particles during sintering. The coatings that have lower ASR tend to also have higher surface resistance. This may be due to the even distribution of the fillers into the bulk of the coating versus segregating onto the surface.

TABLE 4. Selected Results of Surface and Through-Plane Electrical Conductivity Measurements of Composite Coated Samples

Coating Composition		ASR (Ω-cm²)	Sheet Resistance (Ω)
Vol % Fluoropolymer	Vol% Filler(s)		
40% PCTFE	60% Graphite	0.68	4.2
40% PCTFE	40% Graphite, 20% Carbon black	0.97	3.3
40% PCTFE	30% TiC, 30% Graphite	0.27	8.4
50% PCTFE	25% TiC, 25% Graphite	0.11	25
50% PCTFE	50% Graphite	3.3	5.0
50% ETFE	25% TiC, 25% Graphite	0.58	27
50% ETFE	50% Graphite	2.7	20
40% ETFE	60% Graphite	0.75	2.8

Corrosion resistance of coated aluminum samples was measured using electrochemical methods [7] 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, conducted at 80°C, the electrolyte was 0.001M sulfuric acid (pH= 3) with 0.1 ppm NaF. For cathodic corrosion tests, air was bubbled continuously through the acid solution and a potential of 0.6 V vs. Ag/AgCl (0.8 V vs. normal hydrogen electrode, NHE) was applied for 24 h. For anodic corrosion tests, argon was continuously bubbled through the acid solution and a potential of -0.4 V vs. Ag/AgCl (-0.2 V vs. NHE) was applied for 24 h. The results for aluminum plates with a coating of 25 vol% TiC/25% graphite/50 vol% EFTE applied by spraying at Orion Industries are shown in Figure 2. The corrosion current densities for the cathodic tests were below the DOE corrosion target, however, the anodic corrosion current densities were higher than the DOE target.

A total of 75 uncoated aluminum bipolar plates with flow fields have been stamped with a 60 cm^2 active area. The design is based on the GTI patented trapezoidal flow field structure for PEM fuel cells with very low pressure drop. The hydrogen permeability of the formed plates was tested and the results did not show any detectable hydrogen pass-through at 50 psig (3.4 atm), meeting the DOE target. In addition, the cell design was proven during fuel cell testing, and it showed that the stacks can be well sealed against fuel, oxidant, and cooling water leaks. In order to improve electrical conductivity through the samples GTI has

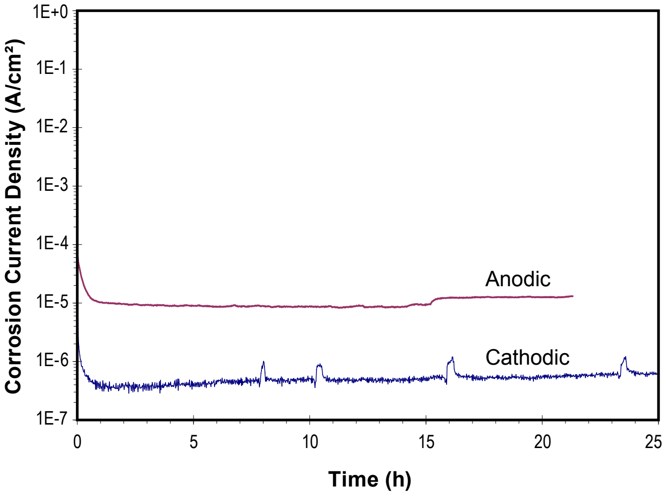

FIGURE 2. Electrochemical Corrosion Test Results for 25% TiC/25% Graphite/50% ETFE on Aluminum Panels Produced by Orion

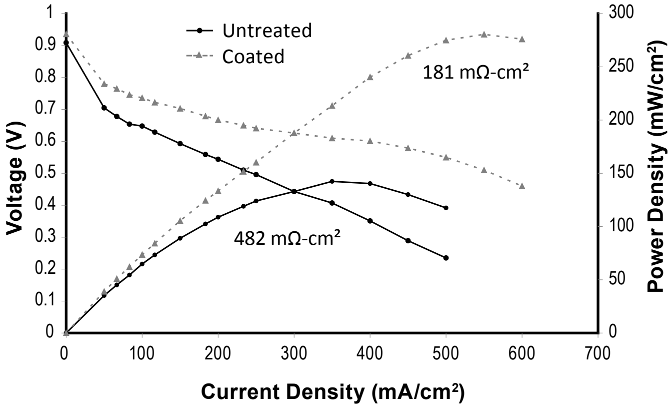

FIGURE 3. Performance Curves for 92% Graphite Coating on Aluminum and Uncoated Aluminum in a Single MEA–Two Bipolar Plate Cell

developed surface treatments that deposit a small amount of metal on the surface of the aluminum before the coating is applied. Two of these treated and coated stamped aluminum plates have been tested in a single-MEA, two-bipolar plate cell at 50°C using a Gore MEA fed with hydrogen and air. The results are shown in Figure 3 and compared to the results obtained with untreated aluminum bipolar plates. The treated and coated aluminum bipolar plates performed better compared to the untreated aluminum bipolar plates. This is because the uncoated aluminum plates had formed a resistive oxide layer on the surface, whereas it was removed and prevented from forming on the treated and coated bipolar plates. Figure 4 shows a photograph of the stamped and coated aluminum plates.

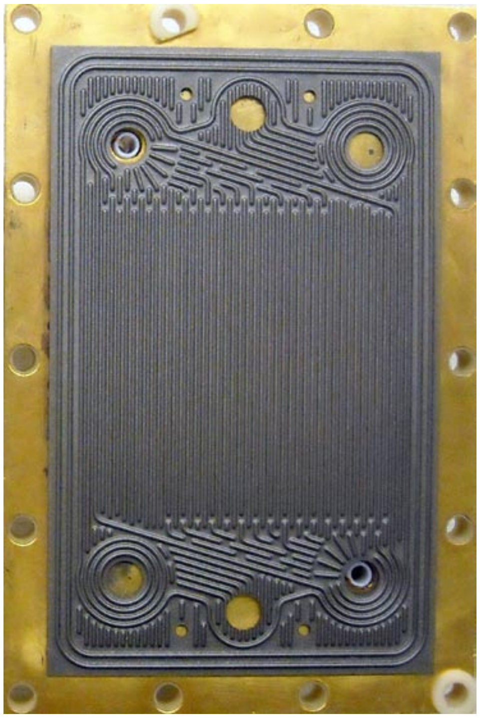

FIGURE 4. Picture of Stamped and Coated Aluminum Bipolar Plate Prior to the Single Cell Test

Conclusions and Future Directions

- Composites made with a combination of flake graphite and nano-size titanium carbide as the filler have the highest electrical conductivities.
- These coatings provide adequate corrosion protection under cathodic conditions.
- Coatings from Orion will be made thinner and with a higher fraction of conductive filler to improve electrical properties.
- Aluminum surface treatments will be evaluated for improved conductivity and corrosion resistance.
- A different fluoropolymer will be evaluated for its potential to improve anodic corrosion resistance.
- A manufacturing cost analysis will be conducted.

FY 2011 Publications/Presentations

1. Jennifer Mawdsley, J. David Carter, Suhas Niyogi, Xiaoping Wang, John Vaughey, and Rasit Koc, "Aluminum bipolar plates with composite coatings for proton exchange membrane fuel cells", to be presented at the American Chemical Society Fall 2011 National Meeting and Exposition, Denver, CO, Aug. 28 – Sept. 1, 2011.

2. A.Akkoyunlu, R. Koc, J. Mawdsley and J.D. Carter, "Synthesis of Submicron-size CaB_6 Powders Using Various Boron Sources", accepted for publication in *Ceramic Engineering and Science Proceedings*.

3. N. Siddiqui, R. Koc, J. Mawdsley and J.D. Carter, "Synthesis of Sub-micron/Nano-sized CaB_6 from Carbon Coated Precursors", accepted for publication in *Ceramic Engineering and Science Proceedings*.

4. R. Duddukuri, R. Koc, J. Mawdsley and J.D. Carter, "Synthesis of Nano-size TiB_2 Powders Using Carbon Coated Precursors", accepted for publication in *Ceramic Engineering and Science Proceedings*.

5. S. Stariha, S. Niyogi, T.K. Honaker-Schroeder, J.D. Carter, and J.R. Mawdsley, "Hydrophilic Surface Treatments for Graphite-Fluoropolymer Composite Coatings on Metallic Bipolar Plates," (Poster) 241st American Chemical Society (ACS) Meeting and Exposition, Anaheim, CA, March 27–31, 2011.

6. N. Siddiqui, R. Koc, J. Mawdsley, and J.D. Carter, "Synthesis of Nano-Size CaB_6 Powders Using Carbon-Coated Precursors," 35th International Conference and Exposition on Advanced Ceramics and Composites (ICACC'11), Daytona Beach, FL, Jan. 23–28, 2011.

7. A. Akkoyunlu, R. Koc, J. Mawdsley, and J. D. Carter, "Synthesis of Nano-Size CaB_6 Powders Using Various Boron Sources," 35th International Conference and Exposition on Advanced Ceramics and Composites (ICACC'11), Daytona Beach, FL, Jan. 23–28, 2011.

8. R. Dudukuri, R. Koc, J. Mawdsley, and J.D. Carter, "Synthesis of Nano-Size TiB_2 Powders Using Carbon-Coated Precursors," 35th International Conference and Exposition on Advanced Ceramics and Composites (ICACC'11), Daytona Beach, FL, Jan. 23–28, 2011.

9. Jennifer Mawdsley, J. David Carter, Suhas Niyogi, Xiaoping Wang, Rasit Koc, Chinbay Fan, and George Osterhout, "Composite-Coated Aluminum Bipolar Plates for PEM Fuel Cells," (Poster) 5th International Conference on Polymer Batteries and Fuel Cells (PBFC-5), Argonne, IL, Aug. 1–5, 2011.

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