Metallic Bipolar Plates with Composite Coatings

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Project ID # FC024

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Overview

Timeline

- Project started: August 1, 2009
- Project ends: Sept. 30, 2011
- Percent complete: 38%

Budget

- Total project funding:
  - DOE: $1697k
  - Contractor: $260k
- Funding received in FY09: $645k
- Funding received in FY10: $486k

Barriers Addressed

- A-Durability
- B-Cost
- D-Water Transport within Stack

Partners

- Gas Technology Institute *(Aluminum stamping, single stack testing)*
- Orion Industries *(Coating application)*
- Southern Illinois University – Carbondale *(Metal boride synthesis)*

Relevance - Project Objectives

- Create a coated aluminum bipolar plate that meets the DOE performance and durability targets for bipolar plates
  - Thinner and more durable than machined graphite bipolar plates
  - Up to 65% lighter than stainless steel

- Develop a composite coating that is electrically conductive and corrosion resistant using a mixture of a fluoropolymer and inorganic filler
  - Filler: metal borides (TiB_2 & CaB_6), graphite, and/or carbon black
  - Fluoropolymer: Ethylene tetrafluoroethylene (EFTE) or Polychlorotrifluoroethylene (PCTFE)

Cross-sectional view

Relevance of this Project to the DOE Hydrogen Program

- Projected benefits of our work:
  - Reduction in the overall stack weight and/or volume
  - Reduction in costs by using scalable and known manufacturing processes
    - Stamping, welding, and spraying are all methods used to mass produce consumer and industrial goods
  - Improved durability of metal plates by developing a corrosion resistant coating
    - Provides a physical barrier to corrosive media
    - Pinhole-free coatings are already manufactured for the chemical handling industry
  - Improved water management within the stack by the development of a hydrophilic surface treatment

Technical Approach

- Explore the use of metal borides and graphite as electrically conductive fillers
  - TiB_2 and CaB_6 have higher conductivities than graphite
  - Determine acid stability of TiB_2 and CaB_6
- Develop methods for making TiB_2 and CaB_6 less expensively than current industrial processes
- Apply the coatings using the established industrial processes for fluoropolymers.
  - Electrostatic spraying and wet spraying
  - These low cost methods and are already accepted by OEM's
- Measure electrical conductivity and corrosion resistance
- Develop methods for making the coating surface hydrophilic

Technical Approach - Milestones

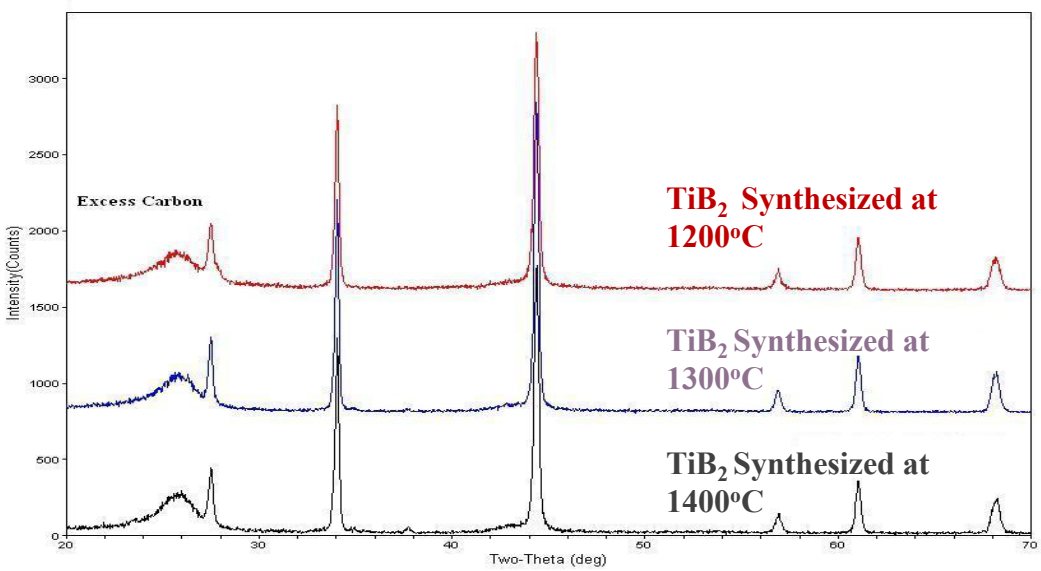
Milestone	Date	Status
Develop a coating that is hydrophilic, conductive, and impermeable to 0.5 M sulfuric acid	September 2009	Completed
Fabricate a composite coated aluminum plate	December 2009	Completed
Synthesize TiB_2 and CaB_6 using proposed low cost process	March 2010	Completed
Finalize the design of the bipolar plate flow fields	March 2010	Completed
Synthesize high-aspect ratio metal boride powders	June 2010	On-track
Fabricate a composite coated Al plate with a electrical conductivity of >100 S/cm, that is corrosion resistant and impermeable to acid solution	September 2010	On-track

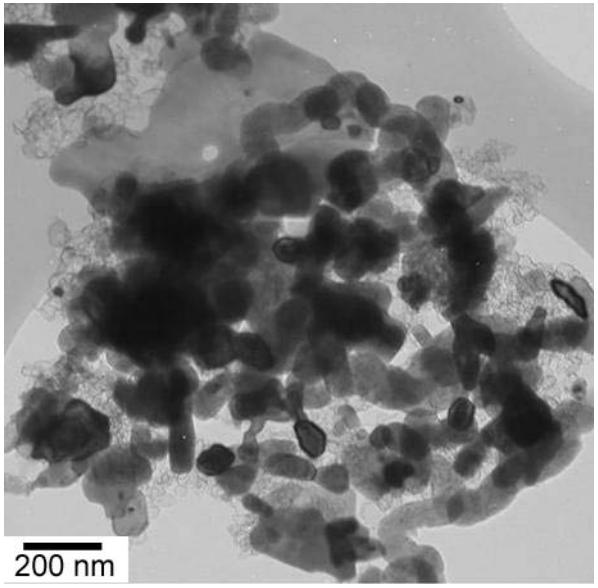
Technical Accomplishments

TiB_2 Powder Synthesized by Low-Cost Process

- Titanium dioxide was uniformly coated with carbon by decomposing propylene (C_3H_6). This coated mixture was then mechanically mixed with the boron carbide (B_4C) and heated to 1200-1400°C in argon.

$$2TiO_2 + B_4C + 3C = 2TiB_2 + 4CO(g)$$

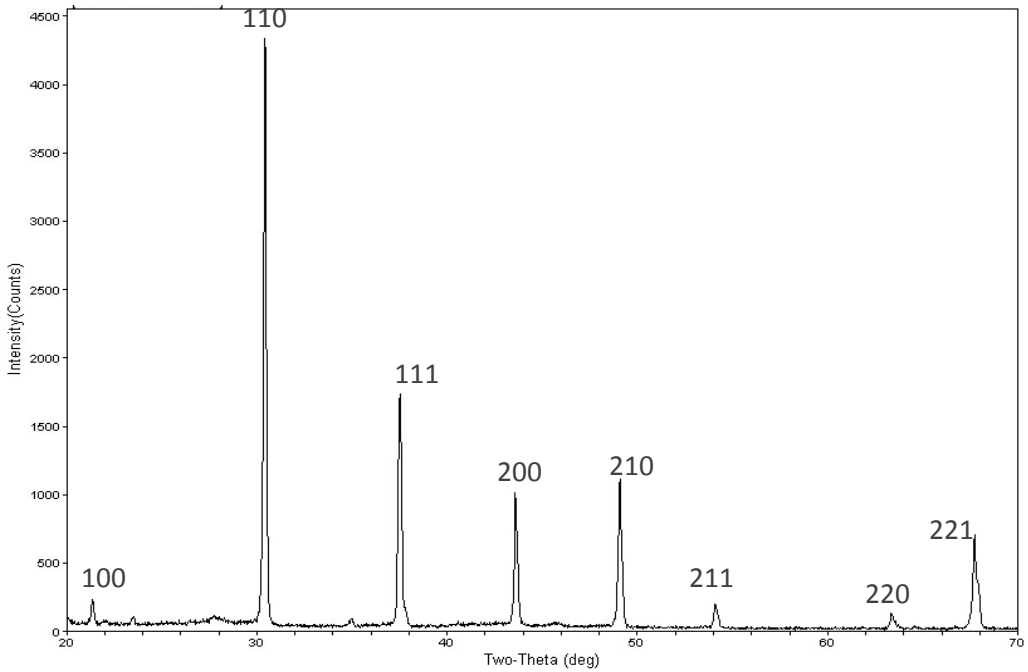


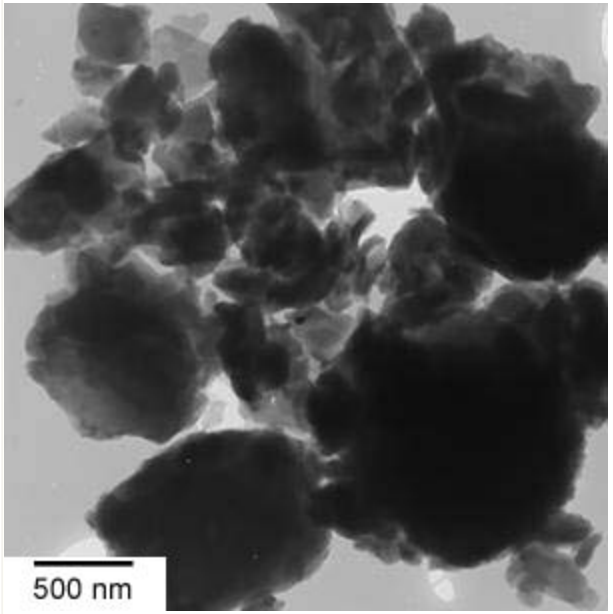


Technical Accomplishments

CaB_6 Powder Synthesized by Low-Cost Process

- Two synthesis methods have been developed to make CaB_6
  - Invention disclosure filed





Technical Accomplishments

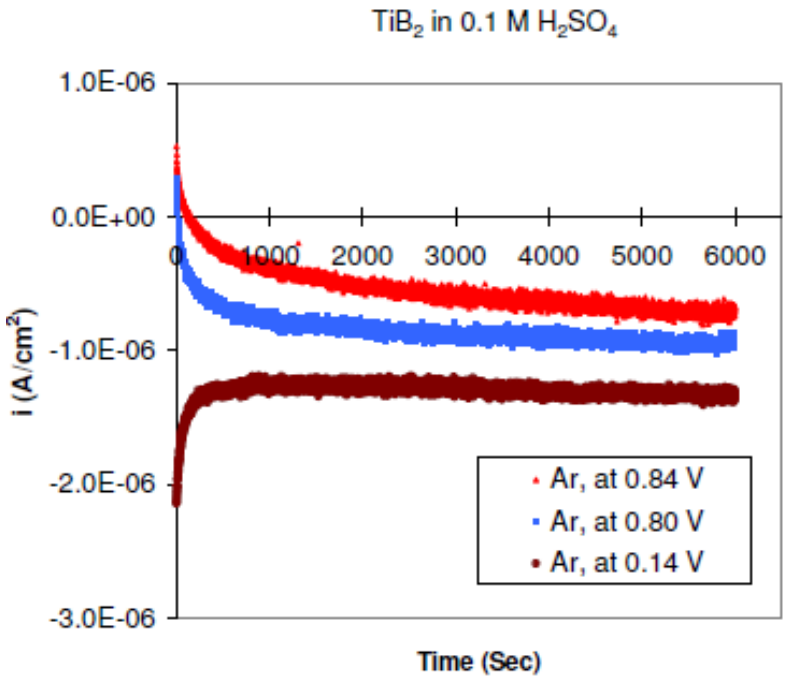
CaB_6 is More Acid Resistant than TiB_2

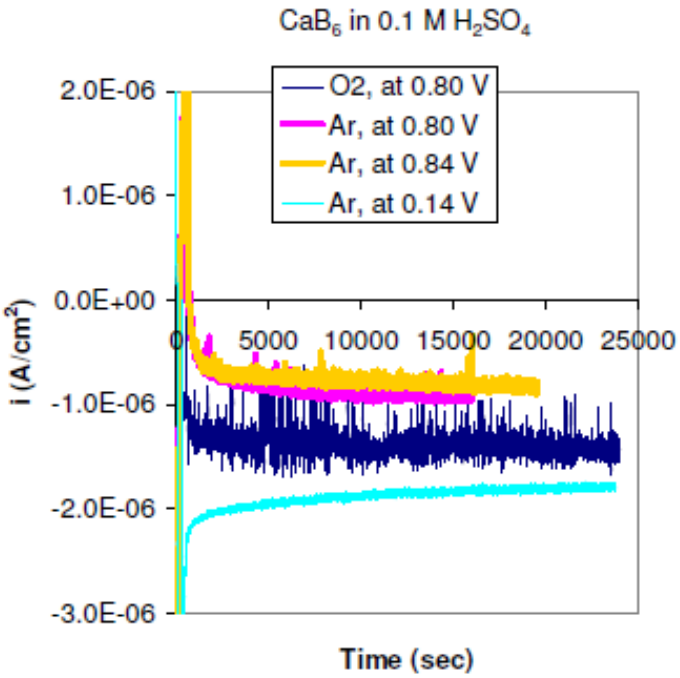
Sample	pH	Time (days)	% Sample Remaining	Extra Phases in XRD
TiB_2 (Cerac, -200 mesh)	1	8	<1	n.a.
TiB_2 (Cerac, -200 mesh)	3	20	77	TiO_2
TiB_2 (SIU)	3	27	95	TiO_2, H_2BO_2, $TiOSO_4$
CaB_6 (Aldrich, -200 mesh)	1	8	131	H_3BO_3
CaB_6 (Aldrich, -200 mesh)	3	15	67	none
CaB_6 (SIU)	3	31	92	none

- Tests conducted at 80°C under reflux conditions in an atmosphere of 3.5% H_2 in He.
- pH = 1: 0.5 M H_2SO_4 with 2 ppm NaF
- pH = 3: 0.001 M H_2SO_4 with 0.1 ppm NaF

Technical Accomplishments
Electrochemical Corrosion of TiB_2 and CaB_6 Studied

- Corrosion testing of TiB_2 and CaB_6 powders was carried out using a standard thin film RDE electrochemical cell with 0.1 M H_2SO_4





- Both TiB_2 and CaB_6 exhibit high corrosion current at potentials relevant to those of PEFC bipolar plates

Technical Accomplishments

Composite Films with Graphite Flake Have the Highest Electrical Conductivity

	Carbon Black	Graphite (spheroidized)	Graphite (flake)	CaB_6	TiB_2
Published Bulk Conductivity (S/cm)	0.1-100[1]	300-2,000[2]		4,500[3]	111,000[3]
Measured Conductivity of Composite (S/cm)	5.0	4.4	26.3	0.57	11.2
Supplier	Cabot	Superior Graphite	Alfa Aesar	Aldrich	Cerac

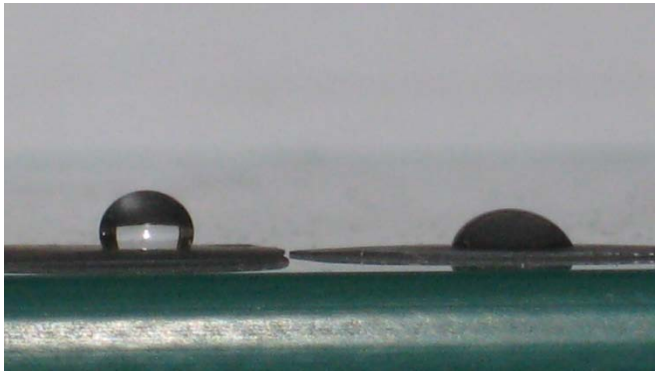
- 60% filler/40% PCTFE films pressed at 235°C
- In-plane measurements made using a 4-point probe (Jandel)

1. *Carbon* **39** (2001) p. 1147–1158; 2. *Engineered Materials Handbook®*, Vol. 4, ASM International (1991); 3. *Handbook of Refractory Compounds*, IFI/Plenum, New York, NY (1980).

Technical Accomplishments

Hydrophilic Surface Treatment Developed

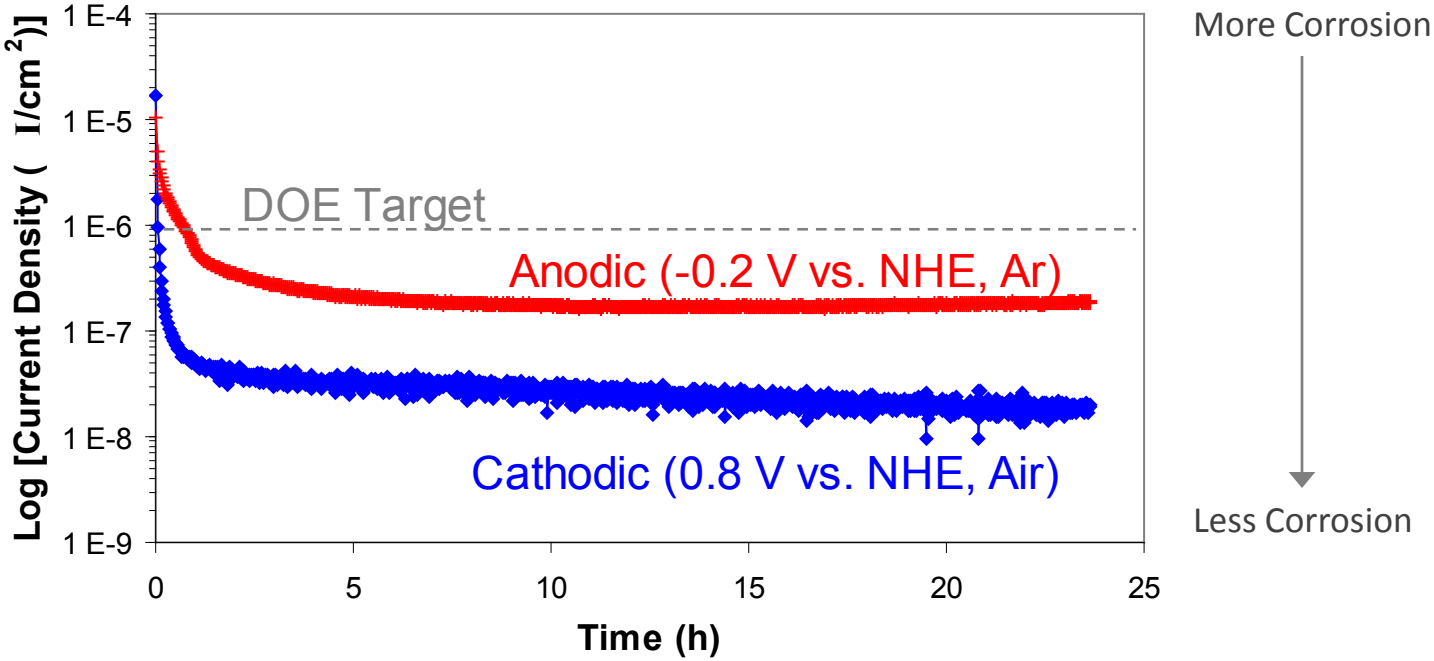
- Two solutions were applied sequentially and the film heated up to 135-150°C for 5 minutes each time.



- Shown in the picture are two samples of 60% graphite/ 40% PCTFE
  - Left side: untreated, contact angle is >90°
  - Right side: treated, contact angle is <90°
- In-plane electrical conductivity increased from 6.7 to 8.9 S/cm

Technical Accomplishments

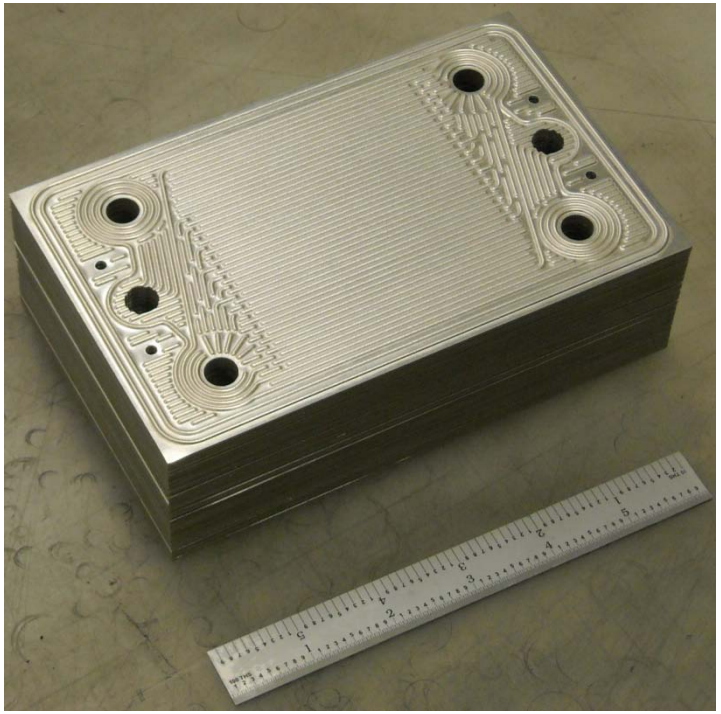
Composite-Coated Aluminum Panels Exceed DOE Bipolar Plate Corrosion Target

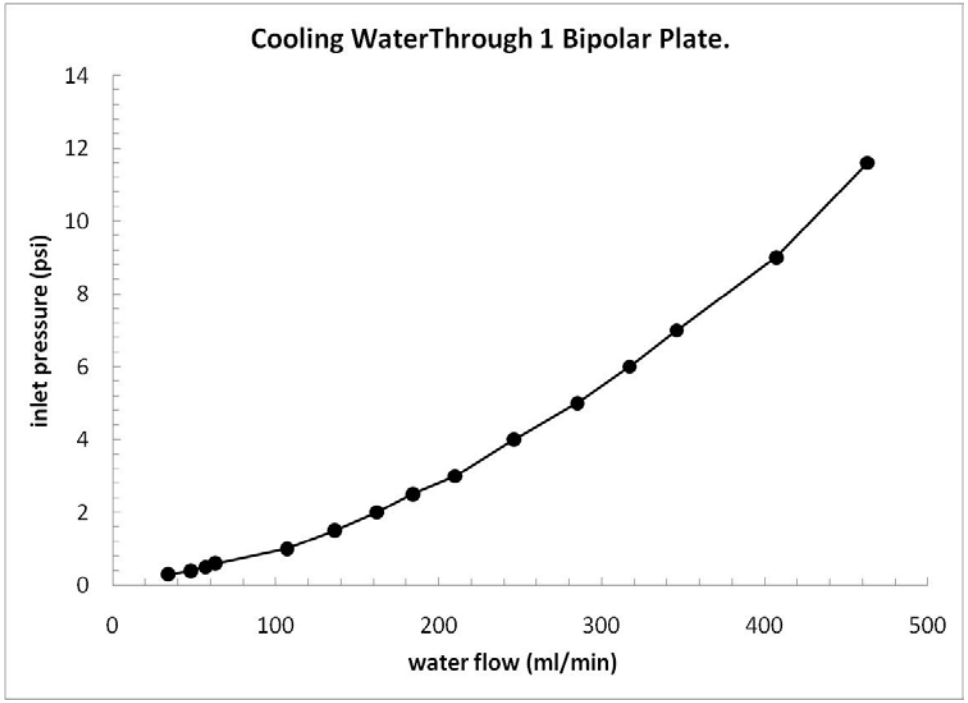


- 20% carbon fiber/80% EFTE coated aluminum panels electrostatically sprayed by Orion Industries
- Potentiostatic tests for 24 hours
  - Electrolyte: 0.001 M H_2SO_4 with 0.1 ppm NaF (pH=3)

Technical Accomplishments

Uncoated Aluminum Plates Stamped and Tested for Hydrogen Permeation



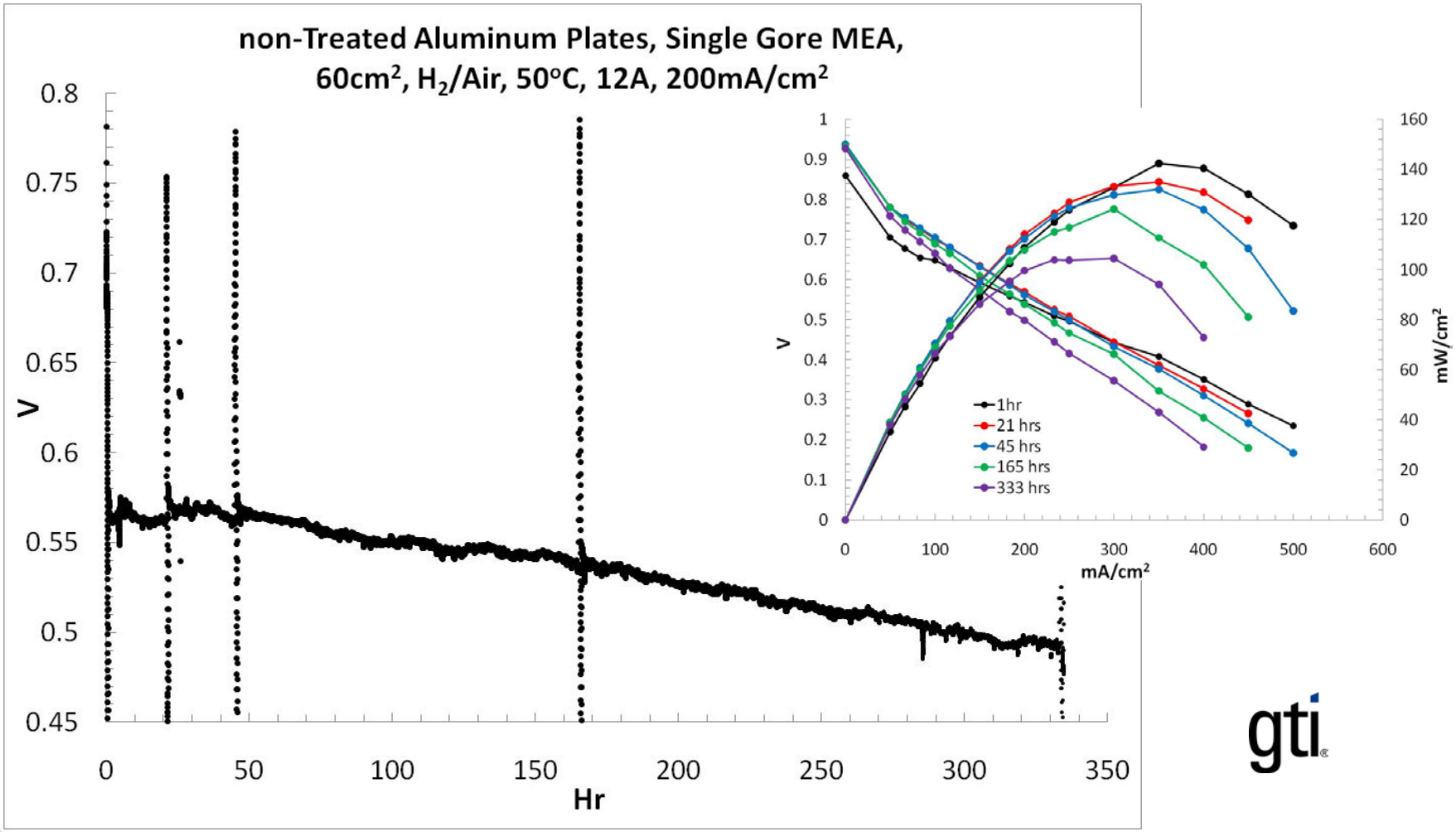


- 100 pieces of pressed aluminum bipolar plates
  - flat and uniform
- Gas flow through plates found to be uniform

- No leakage during water flow testing
- **No hydrogen permeation at 50 psig (3.4 atm) - DOE target met**

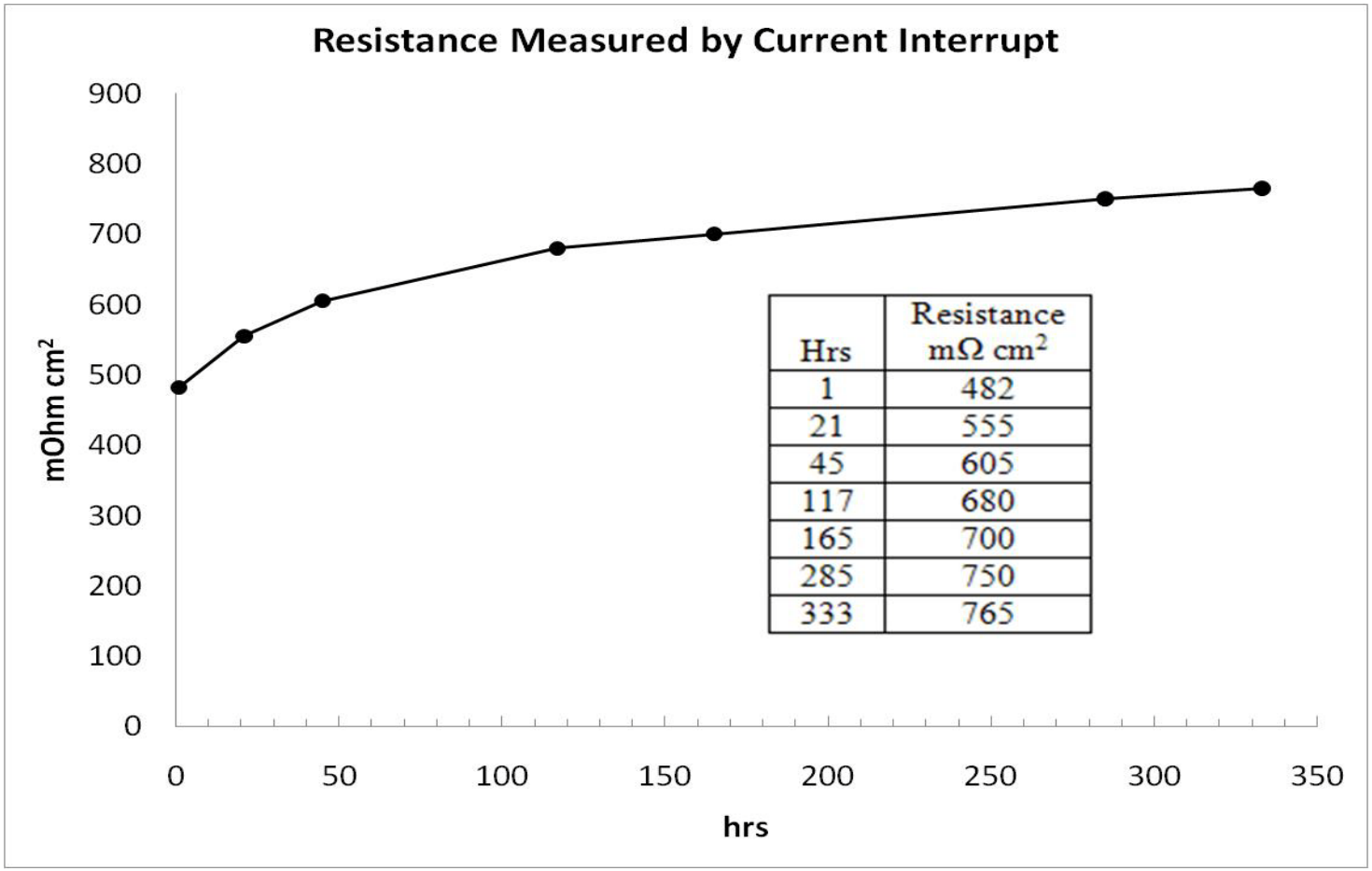
Technical Accomplishments

Single Cell Stack Test of Uncoated Aluminum Plate Shows Voltage and Power Loss with Time



Technical Accomplishments

Resistance of Uncoated Aluminum Plate Increases with Time in Single Cell Test



Hrs	Resistance mΩ cm²
1	482
21	555
45	605
117	680
165	700
285	750
333	765

Collaborations

- Partners:
  - **Gas Technology Institute** (Subcontractor, Industry):
    - Flow field design, aluminum stamping, hydrogen permeation testing and single cell tests
    - Lead Investigator: Dr. Chinbay Fan
  - **Orion Industries** (Subcontractor, Industry):
    - Coating composition and application method
    - Lead Investigator: George Osterhout
  - **Southern Illinois University Carbondale** (Subcontractor, University):
    - Metal boride powder synthesis and characterization
    - Lead Investigator: Prof. Rasit Koc

Proposed Future Work

- Conduct corrosion measurements at 80°C (FY10)
- Conduct contact and through-plane resistance measurements on composite-coated aluminum panels (FY10)
- Continue to improve coating conductivity by looking at alternative filler powders and exploring surface treatments (FY10 & FY11)
- Coat the stamped & welded bipolar plates (FY10 & FY11)
- Conduct single cell testing of coated bipolar plates for up to 2000 hours (FY11)
- Complete a preliminary cost analysis (FY11)

Project Summary

- Relevance
  - Meeting project objectives will reduce weight & cost while improving durability and water management within the stack
- Approach
  - Create a conductive, corrosion resistant composite coating on aluminum
- Technical Accomplishments
  - All project milestones met to date
  - Two DOE targets for bipolar plates met (H_2 permeation & corrosion)
- Collaborations
  - One university and two industrial partners
  - One invention disclosure filed
- Proposed Future Research
  - Improve electrical conductivity of coatings
  - Test coated plates in single cell stack

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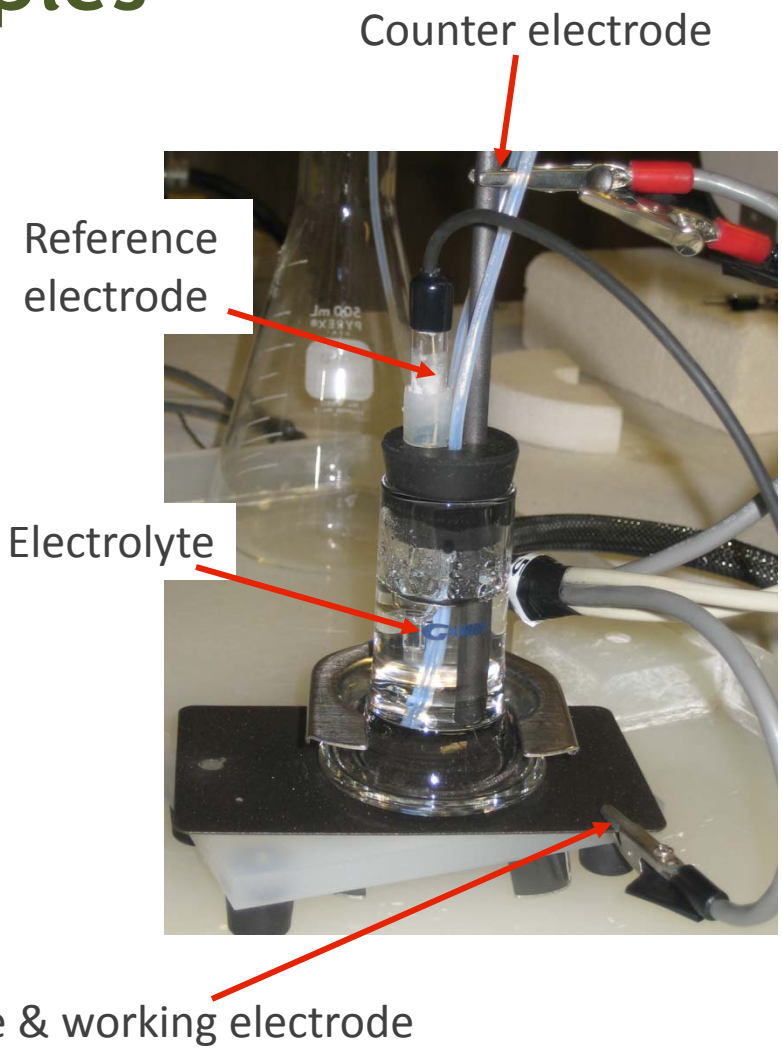
- Ali Akkoyunlu, Mustafa Aydin, Ramesh Duddukuri, Lisa Rajan, Naved Siddique, and George Trifon of the Mechanical Engineering and Energy Processes Department at Southern Illinois University Carbondale

Supplemental Slides

Corrosion Test Set-up For Coated Aluminum Samples

- The test cell is an open ended cylinder
  - The bottom is clamped onto the coated sample and sealed with an o-ring
  - The top is sealed with a stopper that has the reference and counter electrodes fed through, as well as gas inlet and outlet tubing.