# Metallic Bipolar Plates with Composite Coatings

Jennifer Mawdsley (PI), Suhas Niyogi, Xiaoping Wang, and J. David Carter
Argonne National Laboratory

Chinbay Fan
Gas Technology Institute

Prof. Rasit Koc
Southern Illinois University Carbondale

George Osterhout
Orion Industries

May 11, 2011

Project ID # FC024

# Overview

## Timeline

- Project started:  August 1, 2009
- Project ends:  Sept. 30, 2011
- Percent complete:   80%

## Budget

- Total project funding:
  - DOE share: $1697k
  - Contractor share:  $260k
- Funding received in FY10:  $486k
- Funding for FY11 (planned): $566k

## Barriers Addressed

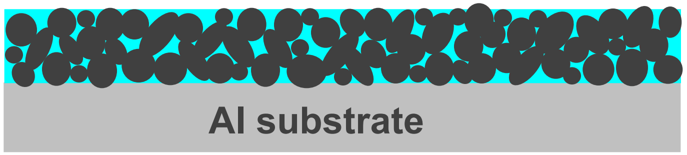
- A-Durability
- B-Cost
- C-Performance

## Partners

- Gas Technology Institute
- Orion Industries
- Southern Illinois University – Carbondale

# 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 carbide, boride or silicide, graphite, and/or carbon black
  - Fluoropolymer: Ethylene tetrafluoroethylene (ETFE) 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

# Technical Approach

- Explore the use of metal borides, carbides, silicides and graphite as electrically conductive fillers
  - $TiB_2$, $CaB_6$, $LaB_6$, TiC and $TiSi_2$ have higher conductivities than graphite
  - Determine acid stability of proposed filler materials
- Develop methods for making metal borides and carbides 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 are already accepted by OEM's
- Measure electrical conductivity and corrosion resistance

# Technical Approach – Milestones

| Milestone | Date | Status |
|---|---|---|
| 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 | Completed |
| Fabricate a composite coated Al plate with a electrical conductivity of >100 S/cm | September 2010 | Completed |
| Finalize the composition of the coating for the single-cell tests | December 2010 | May 31 |
| Begin single-cell tests of composite coated aluminum bipolar plate | March 2011 | June 15 |
| Final cost estimate report for high-volume manufactured cost of the composite coated aluminum bipolar plates | September 2011 | On-Track |

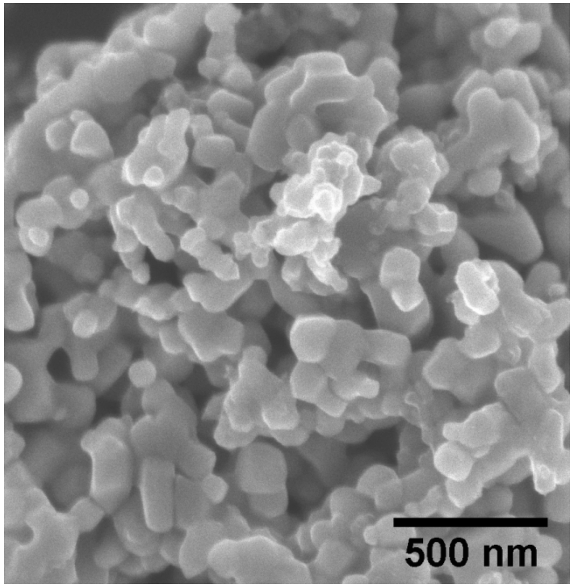
* Previously presented at the 2010 AMR

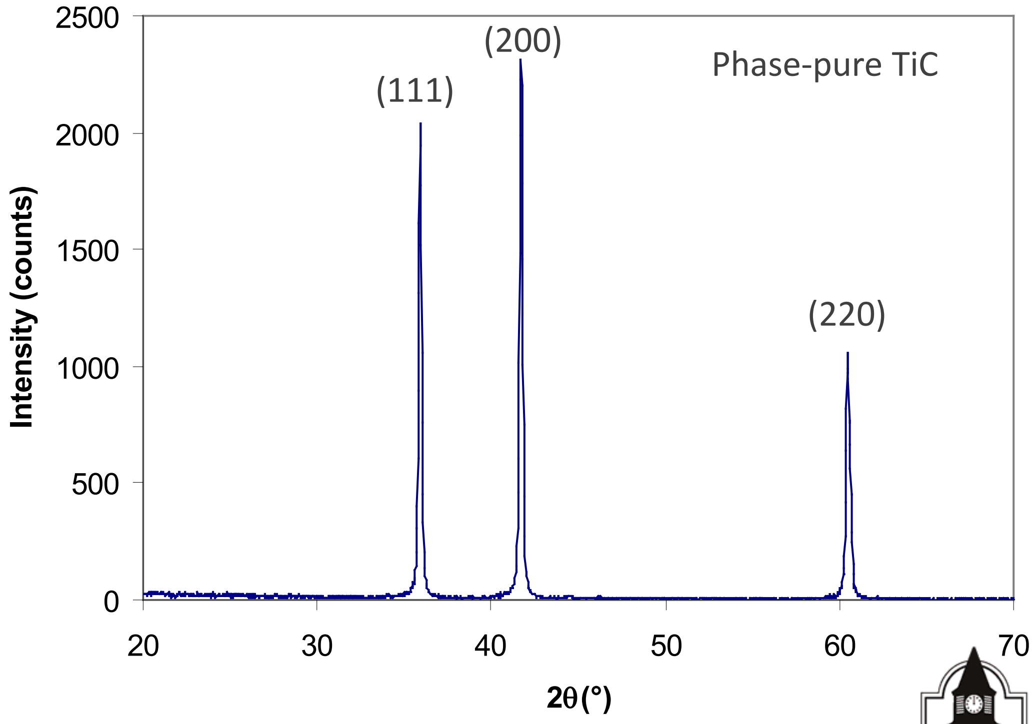
# Titanium Carbide (TiC) Powder Synthesized by Low-Cost Process

- $TiO_2$ coated with carbon by cracking propylene at 550°C over powder from Degussa
- Carbon-coated $TiO_2$ reacted at 1500°C under flowing argon to make TiC:

$$TiO_2(s) + 3C(s) = TiC(s) + 2CO(g)$$

- Process allows the size, morphology, and electronic properties of the powder to be optimized
- Particle size < 200 nm



# Titanium Carbide Has the Best Acid Stability of Candidate Filler Materials as Compared to Graphite

| Sample | Time (days) | % Sample Remaining | Extra Phases in XRD | Ion Concen. (mol/L) |
|---|---|---|---|---|
| TiC (SIU) | 32 | 109% | none | Ti: $<1.3\times10^{-6}$ |
| Flake Graphite (Superior Graphite) | 33 | 94 % | none | n.a. |
| $TiSi_2$ with TiSi & Si impurities (Aldrich) | 30 | 132% | $Ti_3O_5$, $TiO_2$ | Ti: $<1.3\times10^{-6}$<br>Si: $5.6\times10^{-3}$ |
| $LaB_6$ (Aldrich) | 31 | 81 % | none | La: $3\times10^{-4}$<br>B: $1.7\times10^{-3}$ |
| $TiB_2$ (SIU) * | 27 | 95 % | $TiO_2$, $H_2BO_2$, $TiOSO_4$ | Ti: $<1.3\times10^{-6}$<br>B: $9.0\times10^{-2}$ |
| $CaB_6$ (SIU) * | 31 | 92 % | none | Ca: $5.0\times10^{-3}$<br>B: $1.4\times10^{-2}$ |

- Tests conducted at 80°C under reflux conditions in an atmosphere of 3.5% $H_2$ in He.
- 0.001 M $H_2SO_4$ with 0.1 ppm NaF, pH = 3
- Ion concentration in remaining solution determined by ICP-OES
- * Previously presented at the 2010 AMR

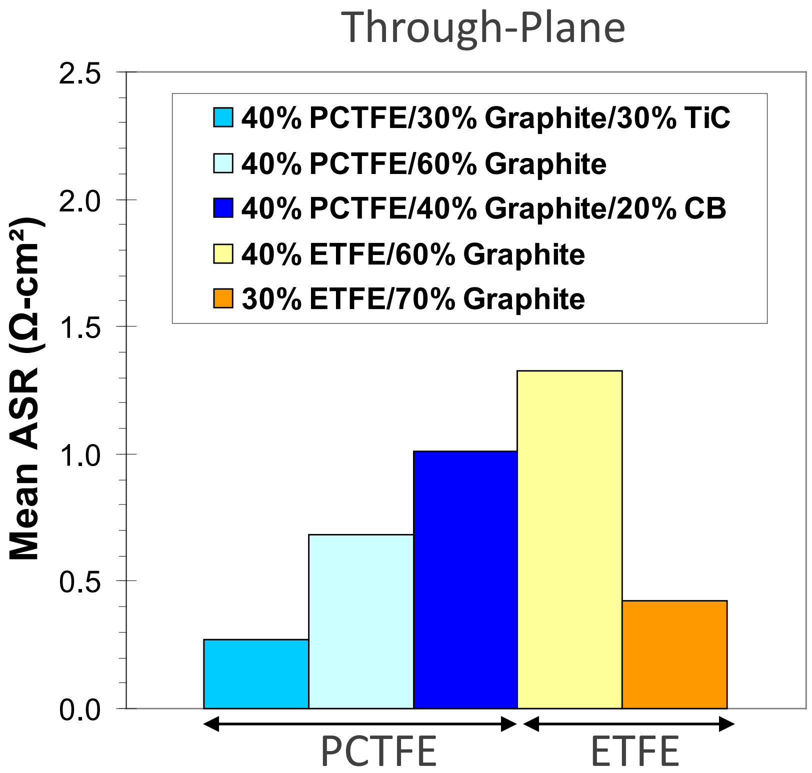
*Technical Accomplishments*

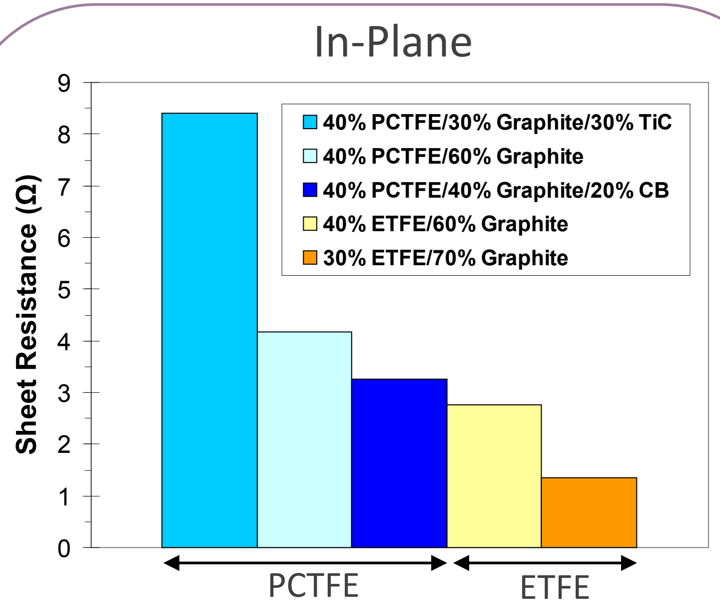
# Electrochemical Corrosion Studies Show That TiC and $TiSi_2$ Are More Stable Than $TiB_2$ and $CaB_6$

| Sample | Corrosion Current ($A/cm^2$) | | | Observations from Cyclic Voltammetry |
|---|---|---|---|---|
| | 0.84 V in Ar | 0.84 V in $O_2$ | 0.14 V in Ar | |
| TiC (SIU) | $6.24 \times 10^{-6}$ | $1.34 \times 10^{-5}$ | $7.06 \times 10^{-6}$ | A small oxidation peak at 0.56 V occurred when cathodic scan went to a potential less than 0.4 V. |
| TiC (Aldrich, milled) | $4.92 \times 10^{-5}$ | $2.87 \times 10^{-5}$ | $2.27 \times 10^{-5}$ | Same features as for unmilled SIU TiC |
| $TiSi_2$ (Aldrich, milled) | $5.65 \times 10^{-6}$ | $5.70 \times 10^{-6}$ | $4.75 \times 10^{-6}$ | No obvious redox features |
| $TiB_2$* | $1.11 \times 10^{-5}$ | $9.41 \times 10^{-6}$ | $7.08 \times 10^{-6}$ | An initial oxidation current in the entire potential range (0 to 1.0 V) gradually decreased until stable CV occurred. |
| $CaB_6$* | $2.44 \times 10^{-5}$ | $2.47 \times 10^{-5}$ | $-3.31 \times 10^{-5}$ | Initial CV showed an oxidation peak at 0.46 V |

- Corrosion testing of TiC, $TiSi_2$, $TiB_2$ and $CaB_6$ powders was carried out using a standard thin film RDE electrochemical cell with 0.1 M $H_2SO_4$ at room temperature
- Both $TiB_2$ and $CaB_6$ exhibit high corrosion current at potentials relevant to those of PEFC bipolar plates
- * Previously presented at the 2010 AMR

# The Composite Coatings Have an Inverse Relationship Between In-Plane and Through-Plane Resistance



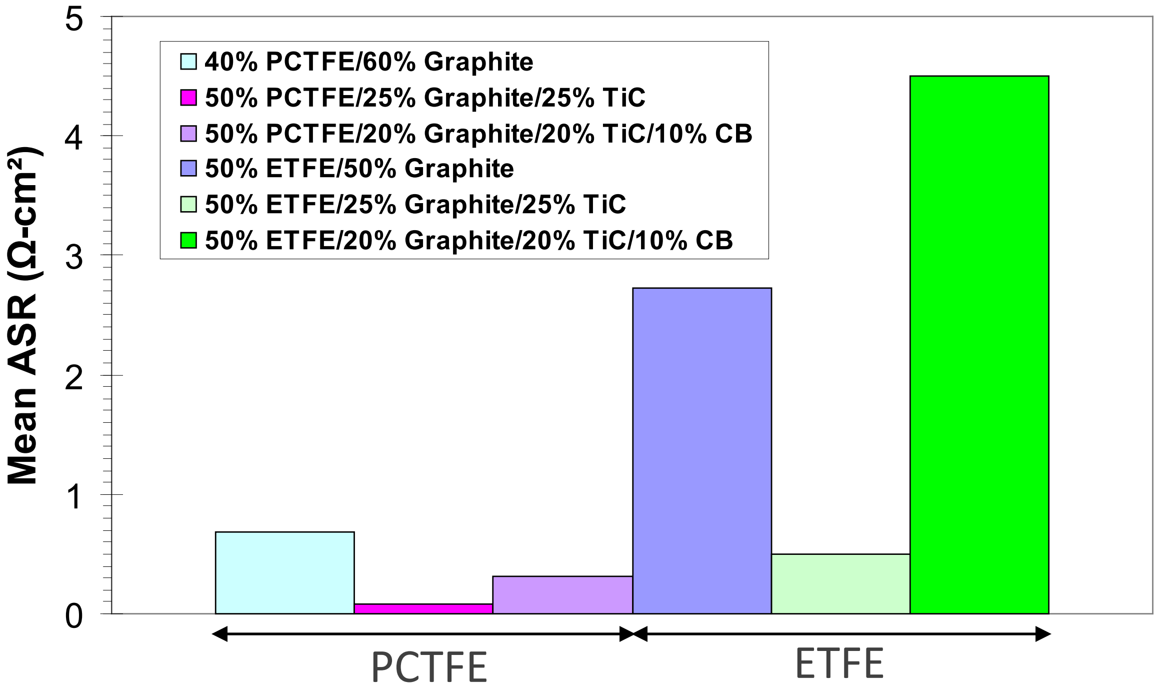




- Coatings sprayed onto ceramic substrates
- In-plane measurements made using a 4-point probe (Jandel) at RT in air

- The target through-plane ASR is 0.02 Ω-cm$^2$
- Through plane measurements taken at an applied load of 142 N/cm$^2$ at RT in air
- Coatings sprayed onto both sides of 6061 or 3003 aluminum substrates
  - Exception: the 30% ETFE/70% Graphite sample was only coated on one side
  - Coatings were 30-130 μm thick on each side

# Composite Films with PCTFE Have Lower Through-Plane Resistance Than Those with ETFE

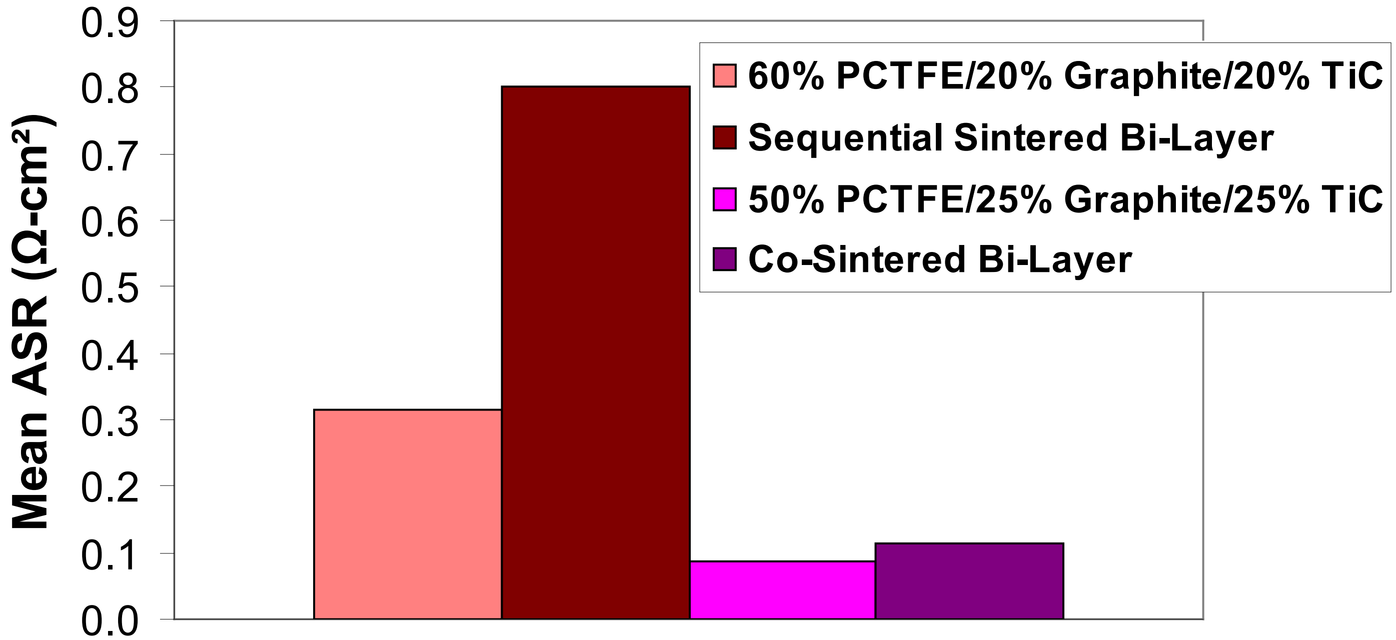
- Substituting TiC for half of the graphite filler lowers the ASR both PCTFE and ETFE coatings




- The target ASR is 0.02 Ω-$cm^2$
- Through plane measurements taken at an applied load of 142 N/$cm^2$ at RT in air
- Used the method described in H.L. Wang, et al., *J. Power Sources,* **115** [2] (2003) 243-251
- Coatings sprayed onto both sides of 6061 or 3003 aluminum substrates
  - Coatings were 30-140 µm thick on each side

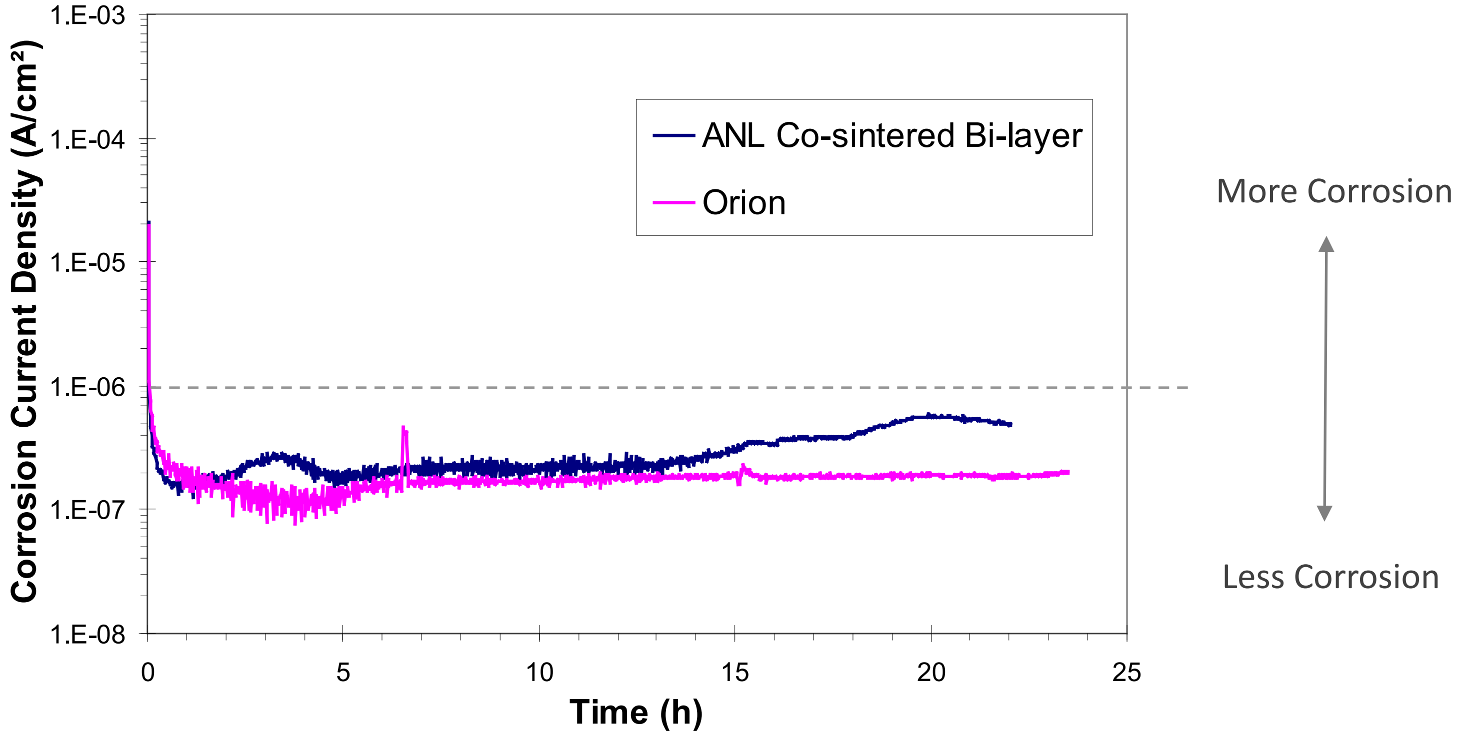
# Bi-Layer PCTFE-Based Coatings Fabricated With Low In-Plane Resistance Top Layer and Low Through-Plane Resistance Bottom  Layer

- Bilayer samples have a top coat of 40% PCTFE/40% graphite/20% carbon black (CB)
  - PCTFE-based composition with the lowest in-plane resistance
- Co-sintered bi-layer PCTFE-based coatings have similar through-plane resistances



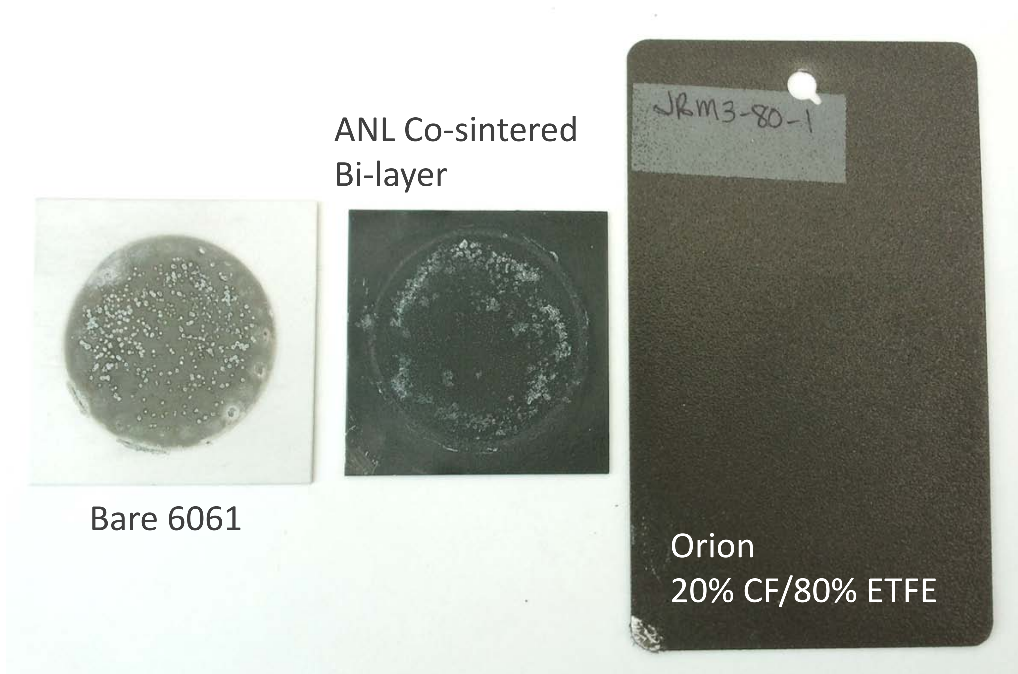

- Coatings sprayed onto both sides of 6061 aluminum substrates
  - Coatings were 60 – 130 μm thick on each side
- Through plane measurements taken at an applied load of 142 $N/cm^2$ at RT in air

# Composite-Coated Aluminum Panels Subjected to Electrochemical Corrosion Tests at 80°C




- Potentiostatic tests for 24 hours at 80°C, purged with air
  - 0.74 V vs. SHE (iR is negligible)
  - Electrolyte: 0.001 M $H_2SO_4$ with 0.1 ppm NaF (pH=3)
- The target corrosion current density is 1 x $10^{-6}$ $A/cm^2$

# Orion's Composite-Coated Aluminum Panels Show No Evidence of Corrosion

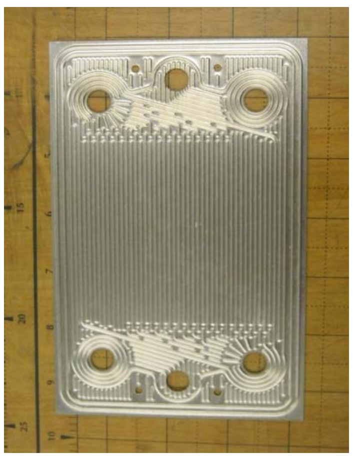


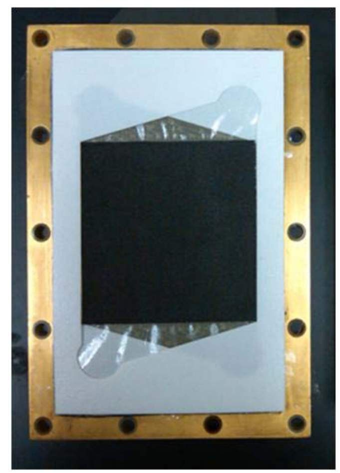

- Co-sintered Bi-layer: Aluminum oxide appears to have percolated up through the coating and deposited on the exposed surface.
  - Coatings did not spall off.
- Orion 20% CF/80% ETFE: No evidence of corrosion

*Technical Accomplishments*

# Coated Aluminum Plates Assembled into Single Cell Stack and Tested

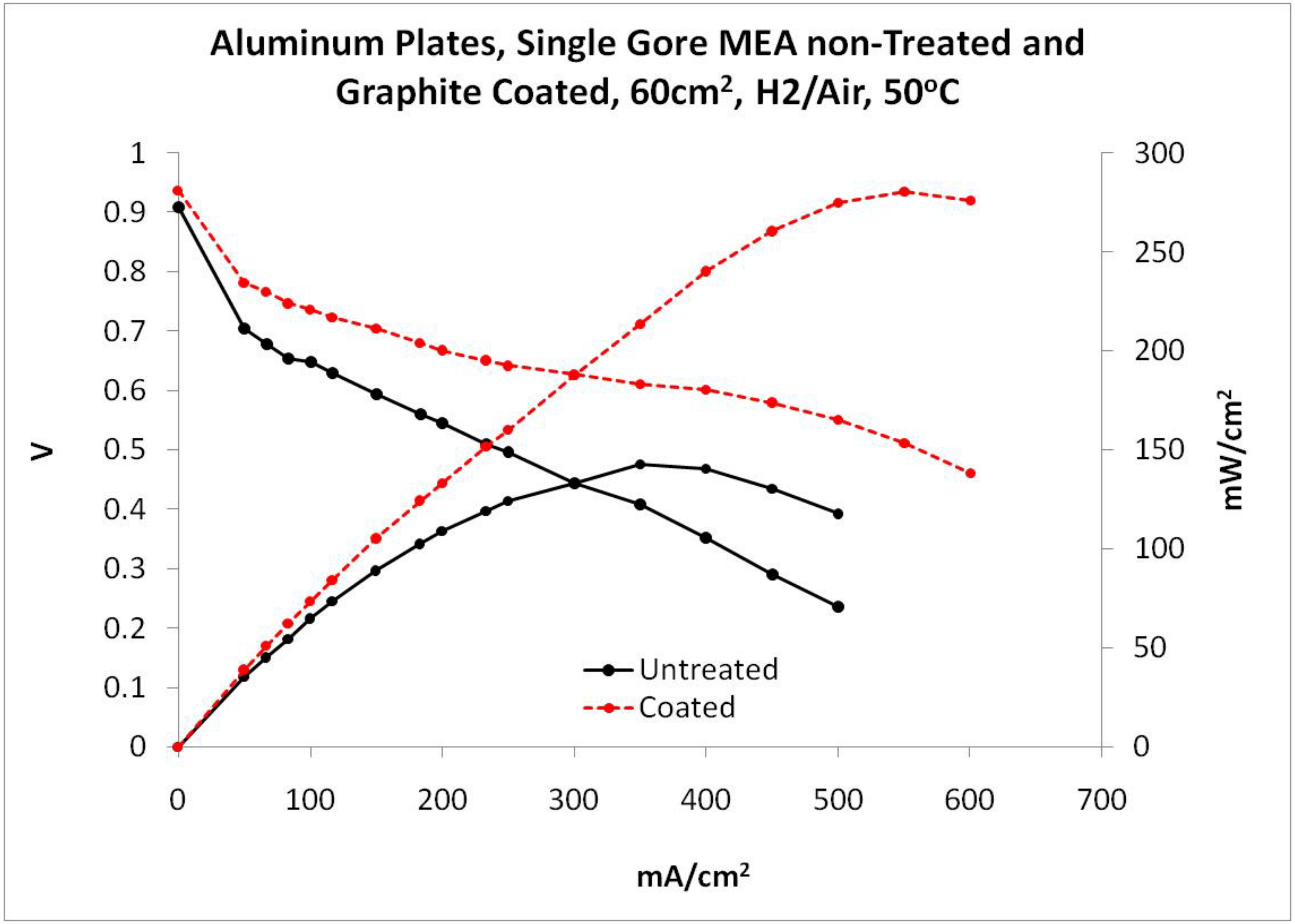
| Material | Surface Resistance (Ω) | Through-Plane Resistance (mΩ) |
|---|---|---|
| Blank Al | 1.964 | 10.52 |
| Composite-Coated Al | 0.175 | 30.5 |





- Active area = 60 cm². The channel depth is 760 μm.
- The gasket is sealed foam polyurethane.
- Dies for a 400 cm² active area plate have been designed.

# Graphite Coated Aluminum Plates Show Improved Performance vs. Uncoated Aluminum Plates



# Collaborations

- Partners:
  - **Gas Technology Institute** (Subcontractor, Industry):
    - Flow field design, aluminum stamping, sealing, 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 and carbide powder synthesis and characterization
    - Lead Investigator: Prof. Rasit Koc

# Proposed Future Work

- Argonne will continue to improve the electrochemical corrosion performance of the coatings by using bi-layer coatings and extending the sintering time
  - A coating composition will be chosen by May 31, 2011
- Orion will coat the GTI stamped & welded bipolar plates with a composite coating developed by Argonne
- GTI will conduct single cell testing of composite-coated bipolar plates for up to 2000 hours
  - Start by June 15, 2011
- Argonne, GTI, Orion and SIU will complete a preliminary cost analysis by Sept. 30, 2011

# 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
  - We expect to meet all project milestones by the end of the project
- Collaborations
  - One university and two industrial partners
  - One invention disclosure filed
- Proposed Future Research
  - Improve electrochemical corrosion protection capabilities of coatings
  - Test coated plates in single cell stack

# Acknowledgements


- Jack Vaughey, Victor Maroni, Debbie Myers, Terry Cruse, Brian Ingram, Nathan Styx, T. Keith Honaker-Schroeder, Sarah Stariha, and Romesh Kumar of the Chemical Sciences and Engineering Division at Argonne National Laboratory

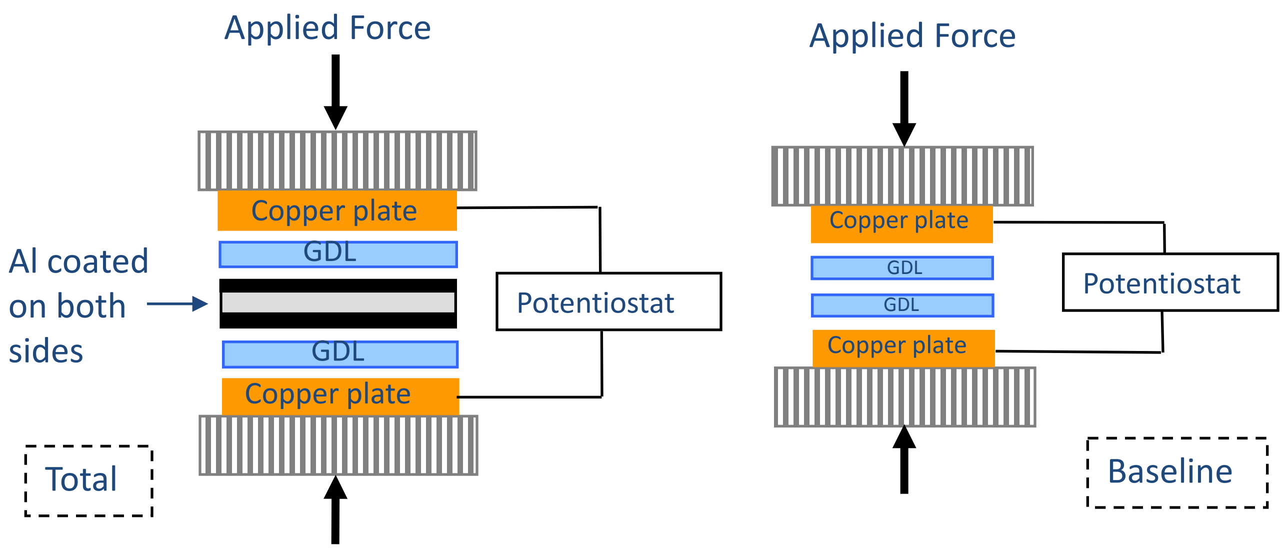
- Don Graczyk, Seema Naik, and Nancy Dietz-Rago of the Analytical Chemistry Laboratory at Argonne National Laboratory

- John Schlueter of the Materials Science Division at Argonne National Laboratory

- Ali Akkoyunlu and Ramesh Dudukuri of the Mechanical Engineering and Energy Processes Department at Southern Illinois University Carbondale

# Technical Back-up Slides

# ASR Measurement Method for Coated Plates

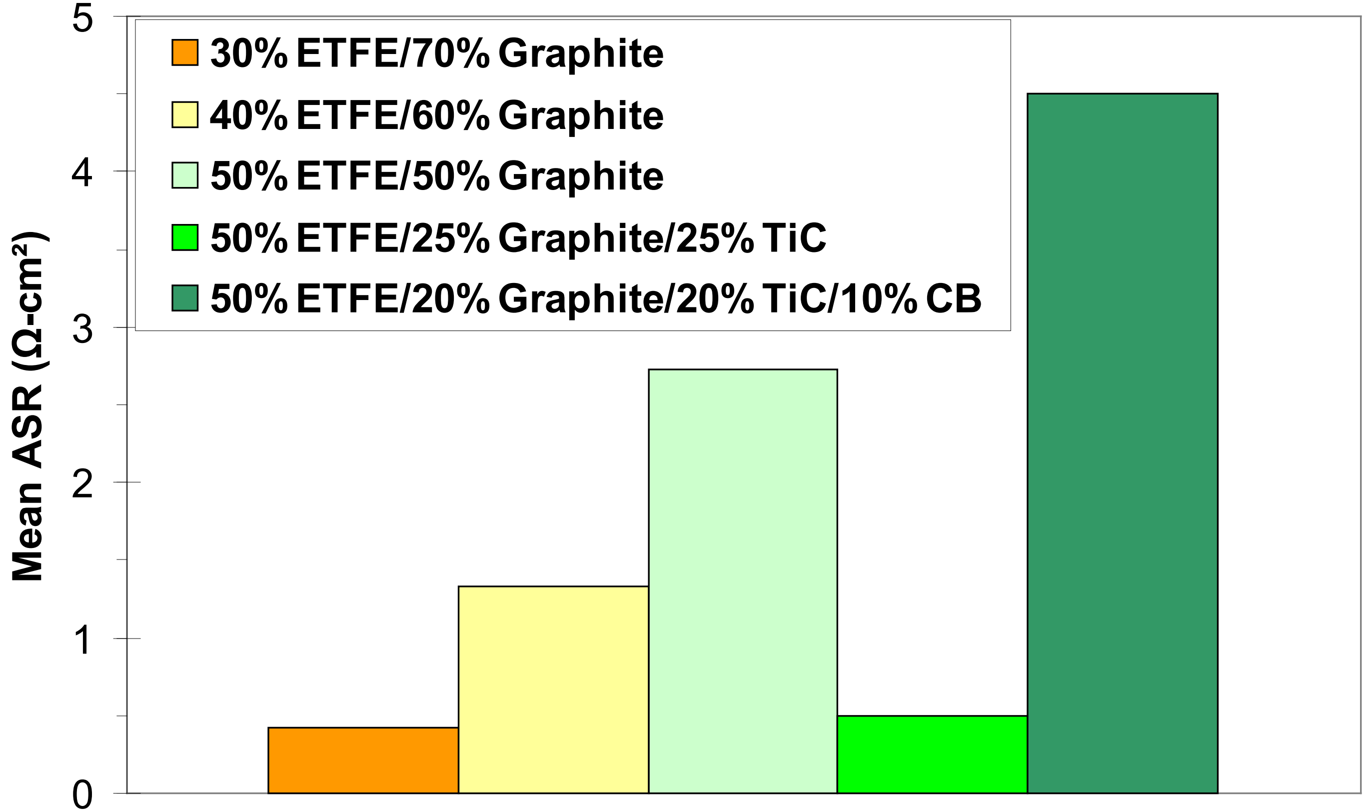



$$ASR_{sample} = (R_{total} - R_{baseline})*area$$

- The GDL used for our tests was Toray™ carbon paper, 110 μm thick.
  - Pre-conditioned by applying a load of 318 psi (219 N/cm²)
- References:
  - H.L. Wang, et al., *J. Power Sources,* **115** [2] (2003) 243-251
  - U.S. Fuel Cell Council, "Electrical Conductivity Testing Protocol" (2004).

*Technical Accomplishments*

# Addition of Titanium Carbide to ETFE-Based Coatings Lowers Through-Plane Resistance




- Coatings sprayed onto both sides of 6061 or 3003 aluminum substrates
- Through plane measurements taken at an applied load of 142 $N/cm^2$