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: 80%

Budget

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

Barriers Addressed

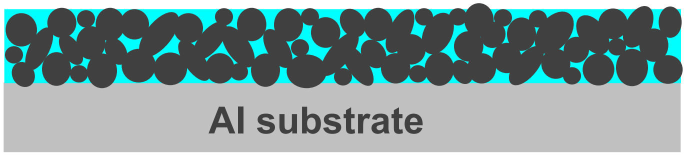
- A-Durability
- B-Cost
- C-Performance

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

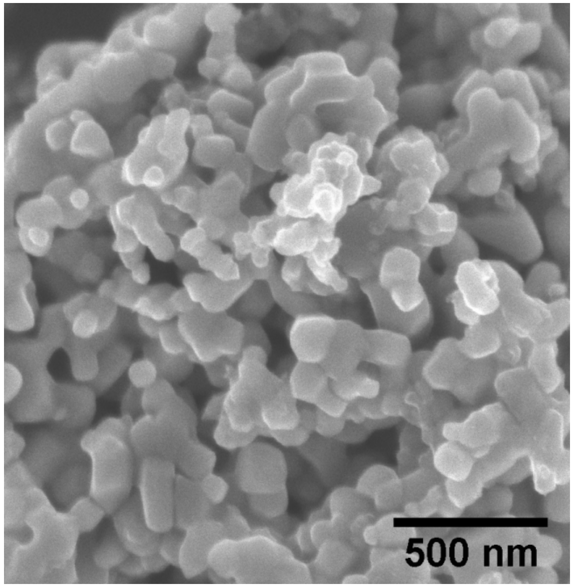
* Previously presented at the 2010 AMR

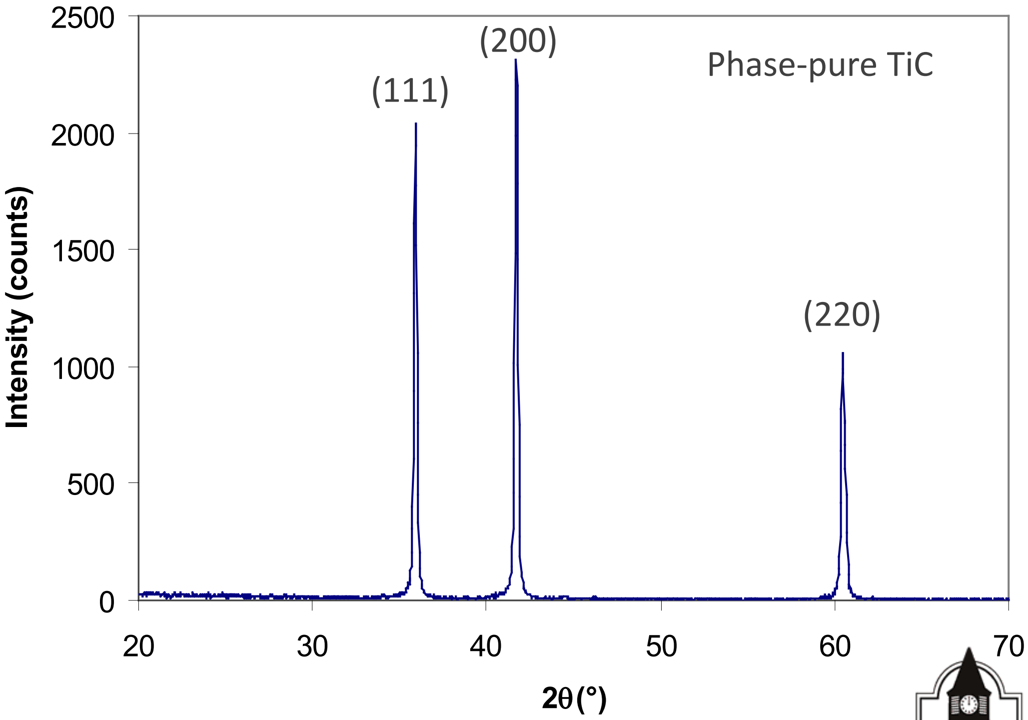
Titanium Carbide (TiC) Powder Synthesized by Low-Cost Process

- 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: <$1.3x10^{-6}$
Flake Graphite (Superior Graphite)	33	94 %	none	n.a.
$TiSi_2$ with TiSi & Si impurities (Aldrich)	30	132%	Ti_3O_5, TiO_2	Ti: <$1.3x10^{-6}$ Si: $5.6x10^{-3}$
LaB_6 (Aldrich)	31	81 %	none	La: $3x10^{-4}$ B: $1.7x10^{-3}$
TiB_2 (SIU) *	27	95 %	TiO_2, H_2BO_2, $TiOSO_4$	Ti: <$1.3x10^{-6}$ B: $9.0x10^{-2}$
CaB_6 (SIU) *	31	92 %	none	Ca: $5.0x10^{-3}$ B: $1.4x10^{-2}$

- 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

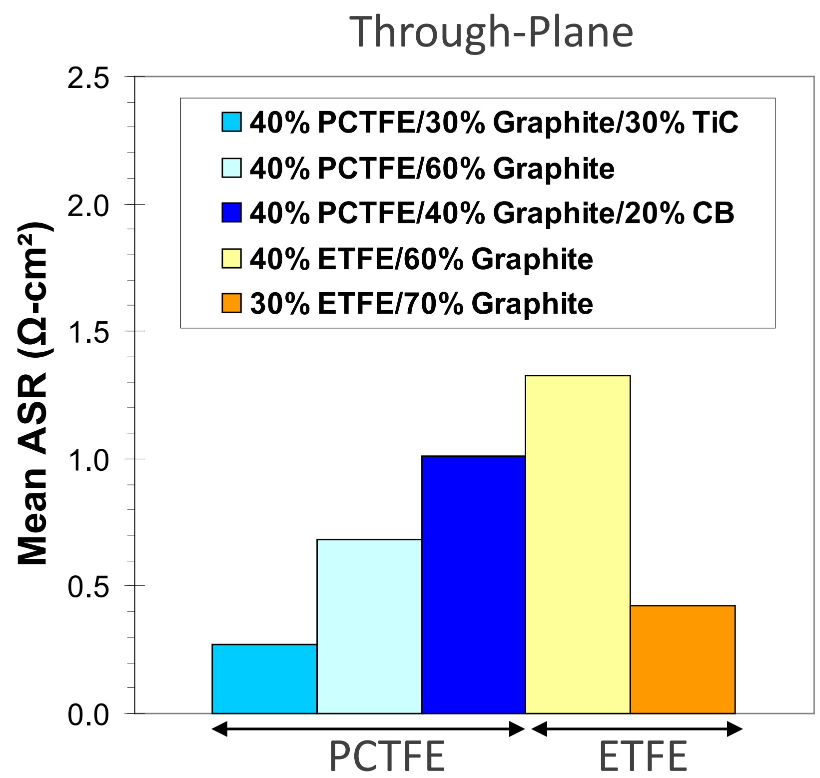
Technical Accomplishments

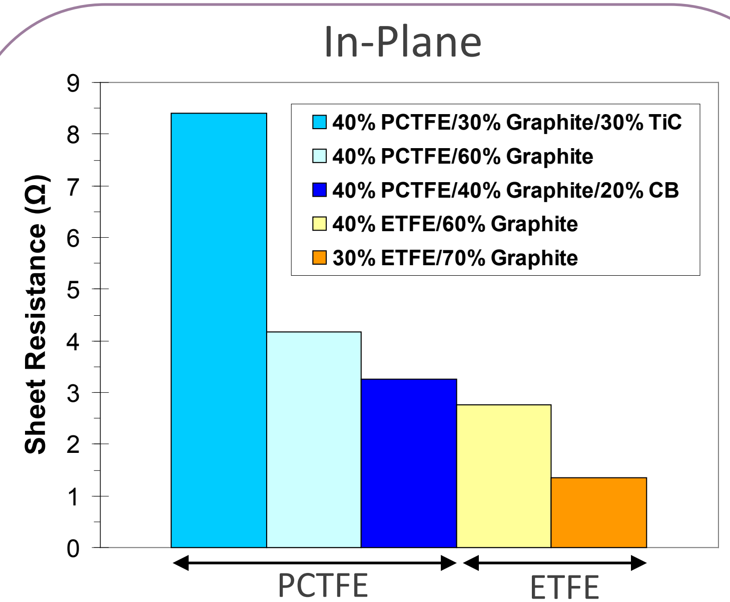
Electrochemical Corrosion Studies Show That TiC and $TiSi_2$ Are More Stable Than TiB_2 and CaB_6

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)	6.24×10^{-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
TiB_2*	1.11×10^{-5}	9.41×10^{-6}	7.08×10^{-6}	An initial oxidation current in the entire potential range (0 to 1.0 V) gradually decreased until stable CV occurred.
CaB_6*	2.44×10^{-5}	2.47×10^{-5}	-3.31×10^{-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



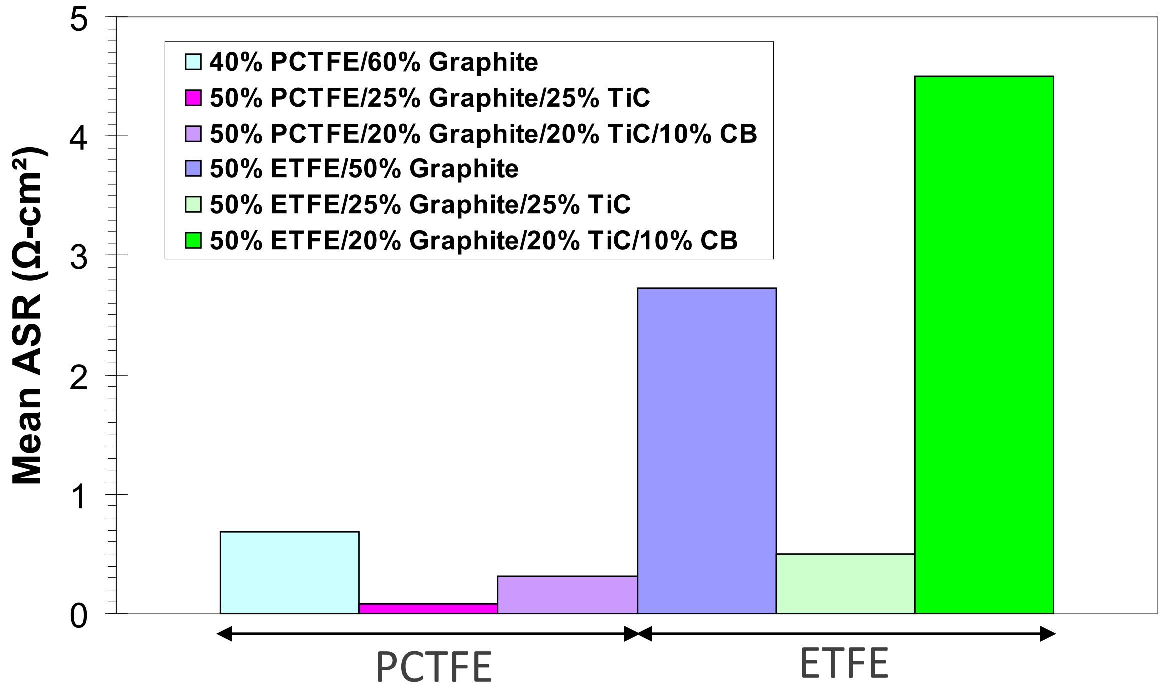


- Coatings sprayed onto ceramic substrates
- In-plane measurements made using a 4-point probe (Jandel) at RT in air

- The target through-plane ASR is 0.02 Ω-cm²
- Through plane measurements taken at an applied load of 142 N/cm² 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

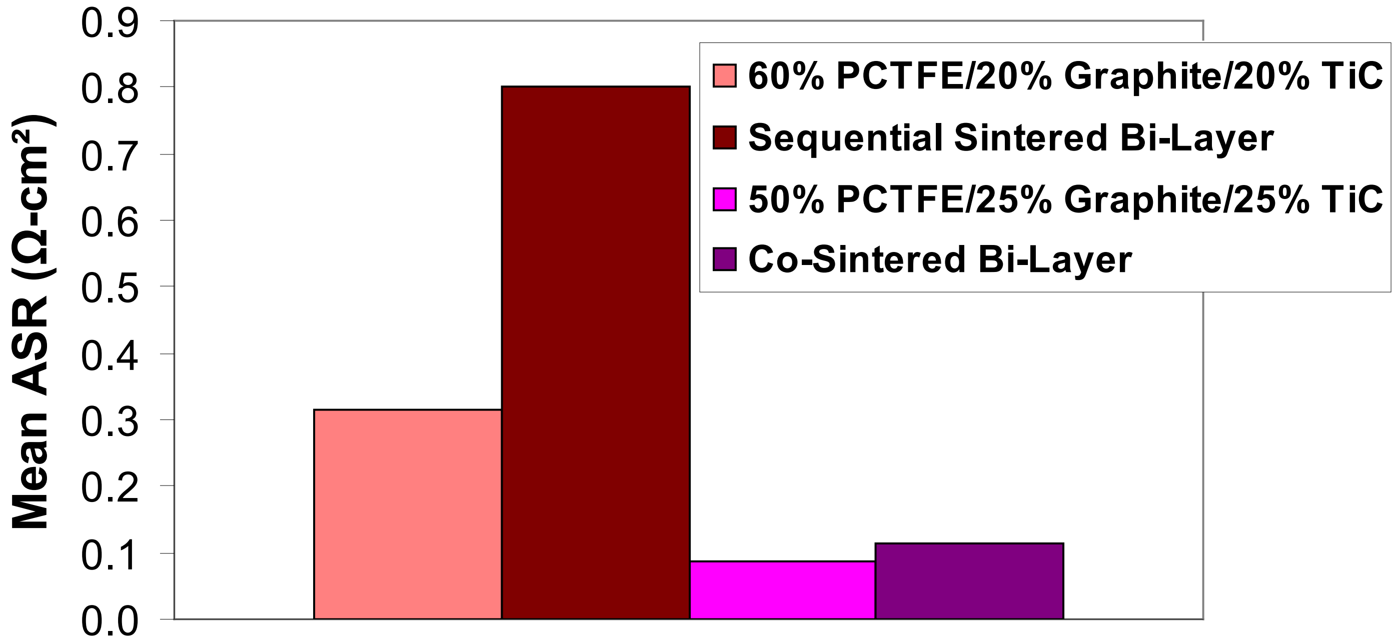


- The target ASR is 0.02 Ω-cm^2
- Through plane measurements taken at an applied load of 142 N/cm^2 at RT in air
- Used the method described in H.L. Wang, et al., *J. Power Sources,* **115** [2] (2003) 243-251
- Coatings sprayed onto both sides of 6061 or 3003 aluminum substrates
  - Coatings were 30-140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

Technical Accomplishments

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

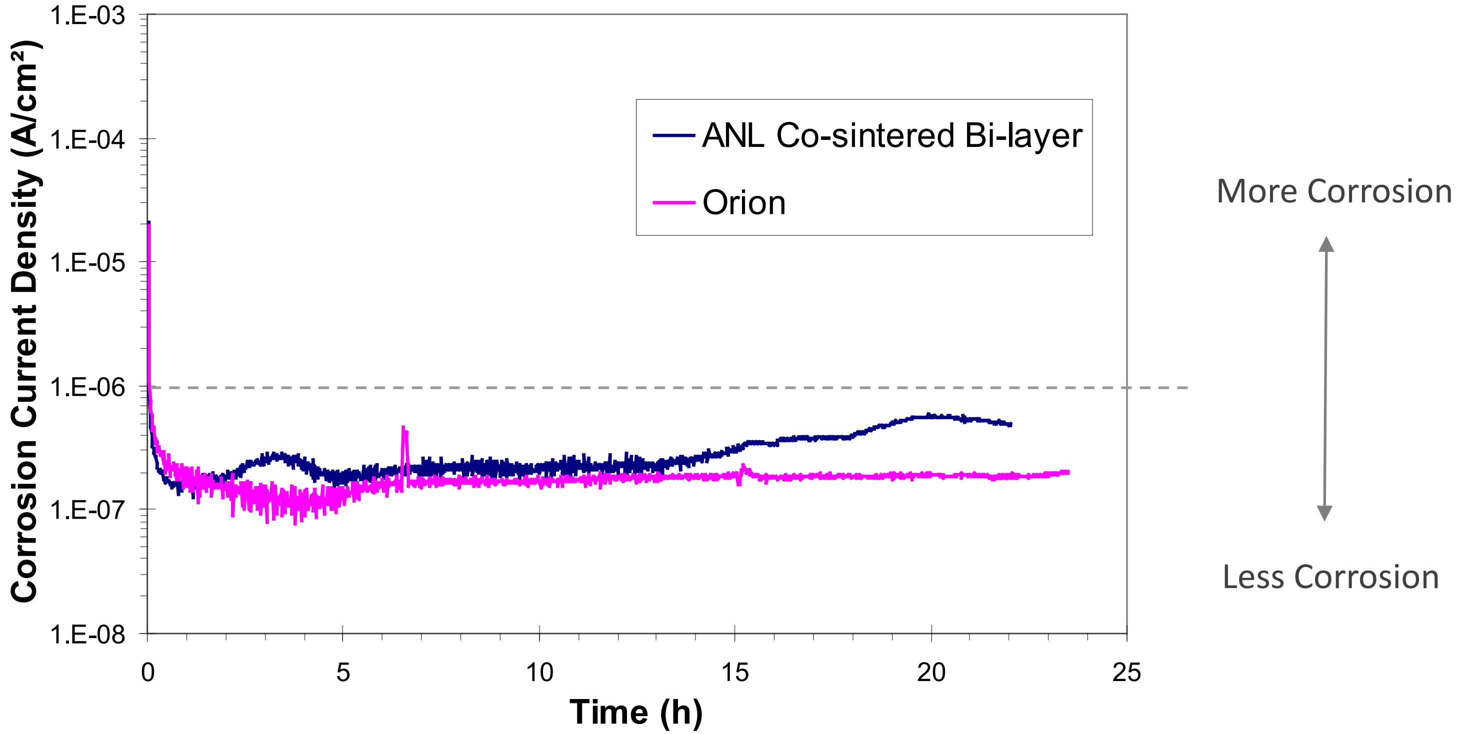
- Bilayer samples have a top coat of 40% PCTFE/40% graphite/20% carbon black (CB)
  - PCTFE-based composition with the lowest in-plane resistance
- Co-sintered bi-layer PCTFE-based coatings have similar through-plane resistances



- 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

Technical Accomplishments

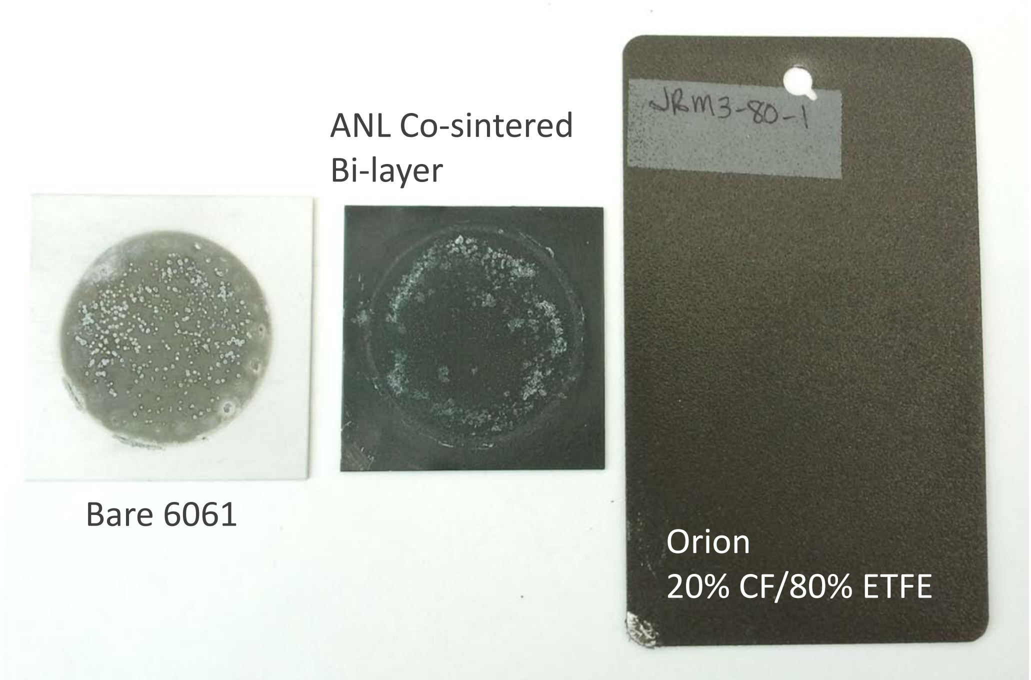
Composite-Coated Aluminum Panels Subjected to Electrochemical Corrosion Tests at 80 °C



- 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/cm²

Technical Accomplishments

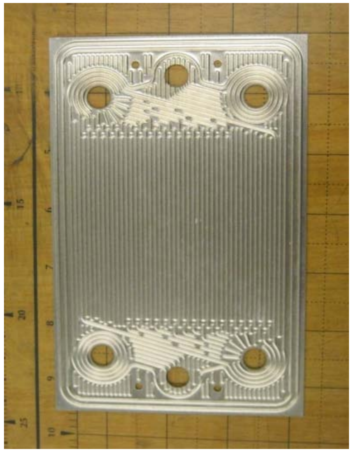
Orion's Composite-Coated Aluminum Panels Show No Evidence of Corrosion



- 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

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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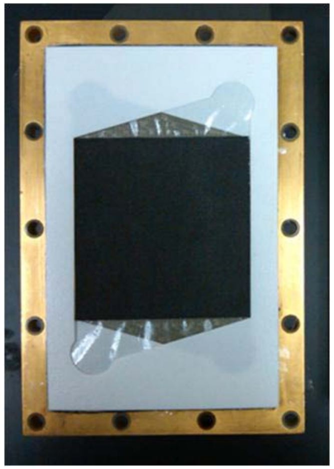
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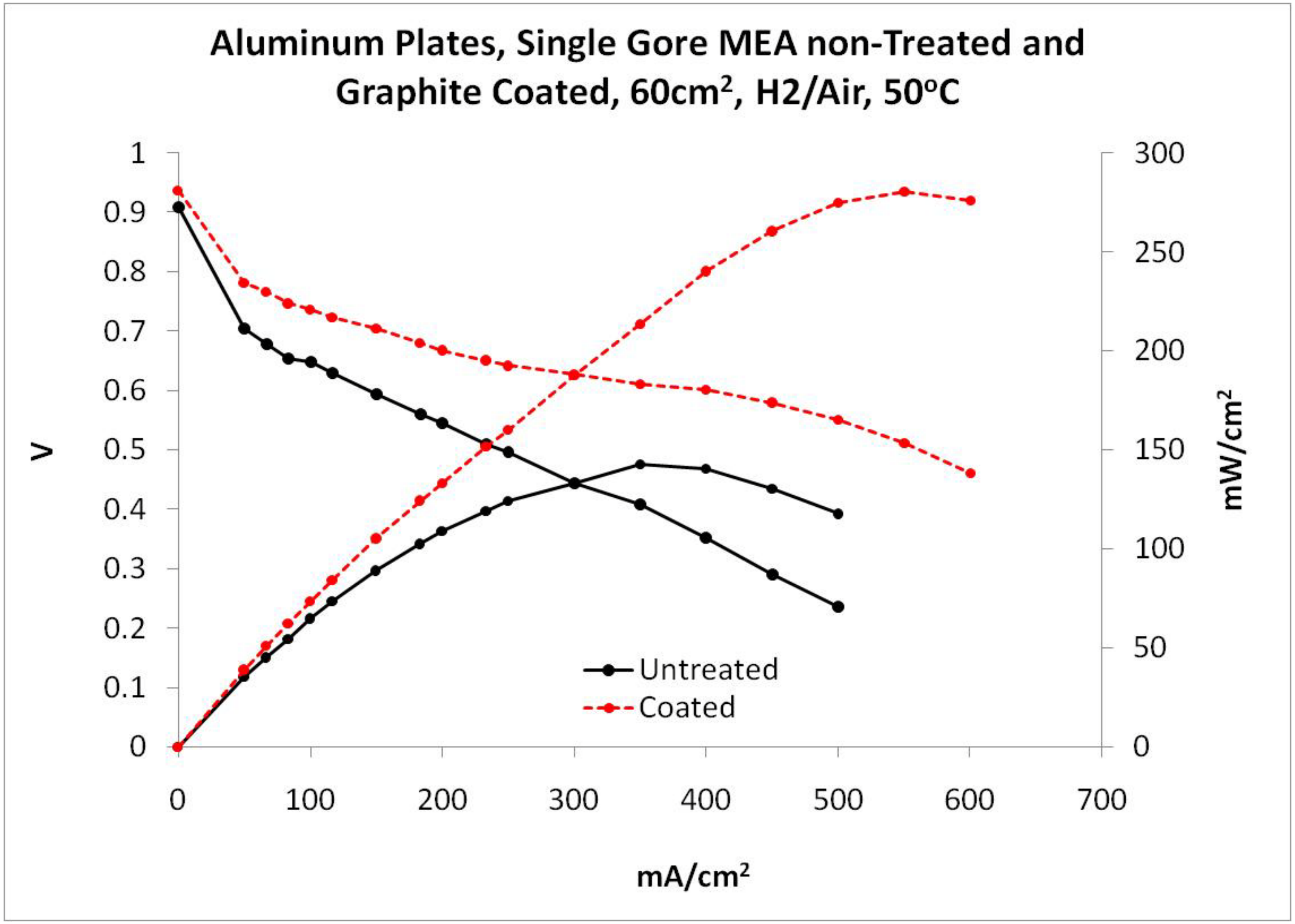
- Active area = 60 cm^2. The channel depth is 760 μm.
- The gasket is sealed foam polyurethane.
- Dies for a 400 cm^2 active area plate have been designed.

Technical Accomplishments

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

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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

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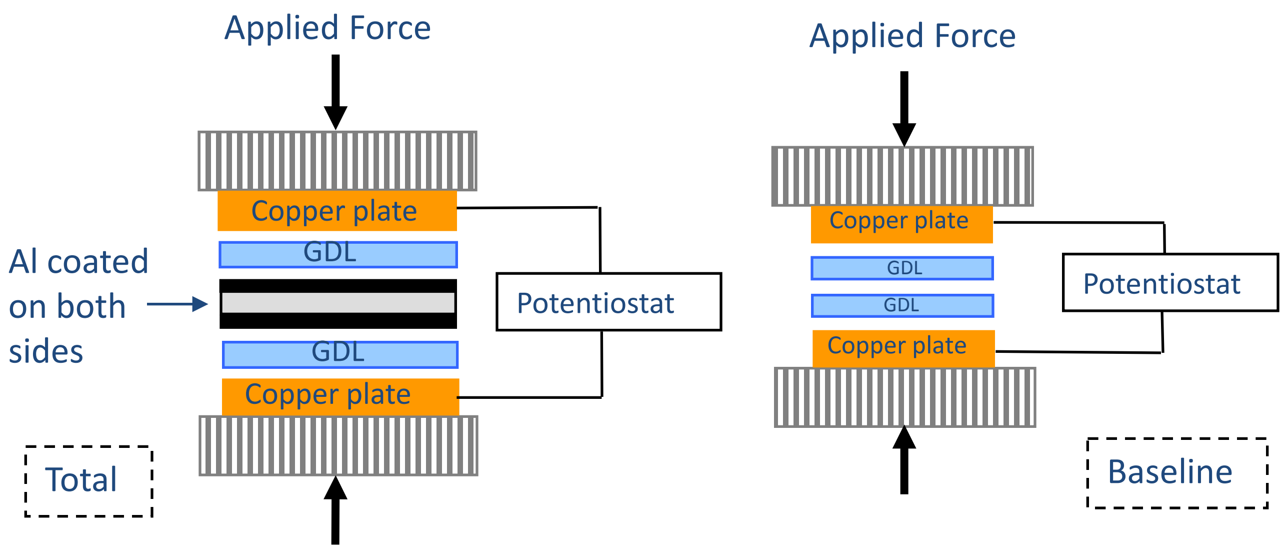
Technical Back-up Slides

ASR Measurement Method for Coated Plates

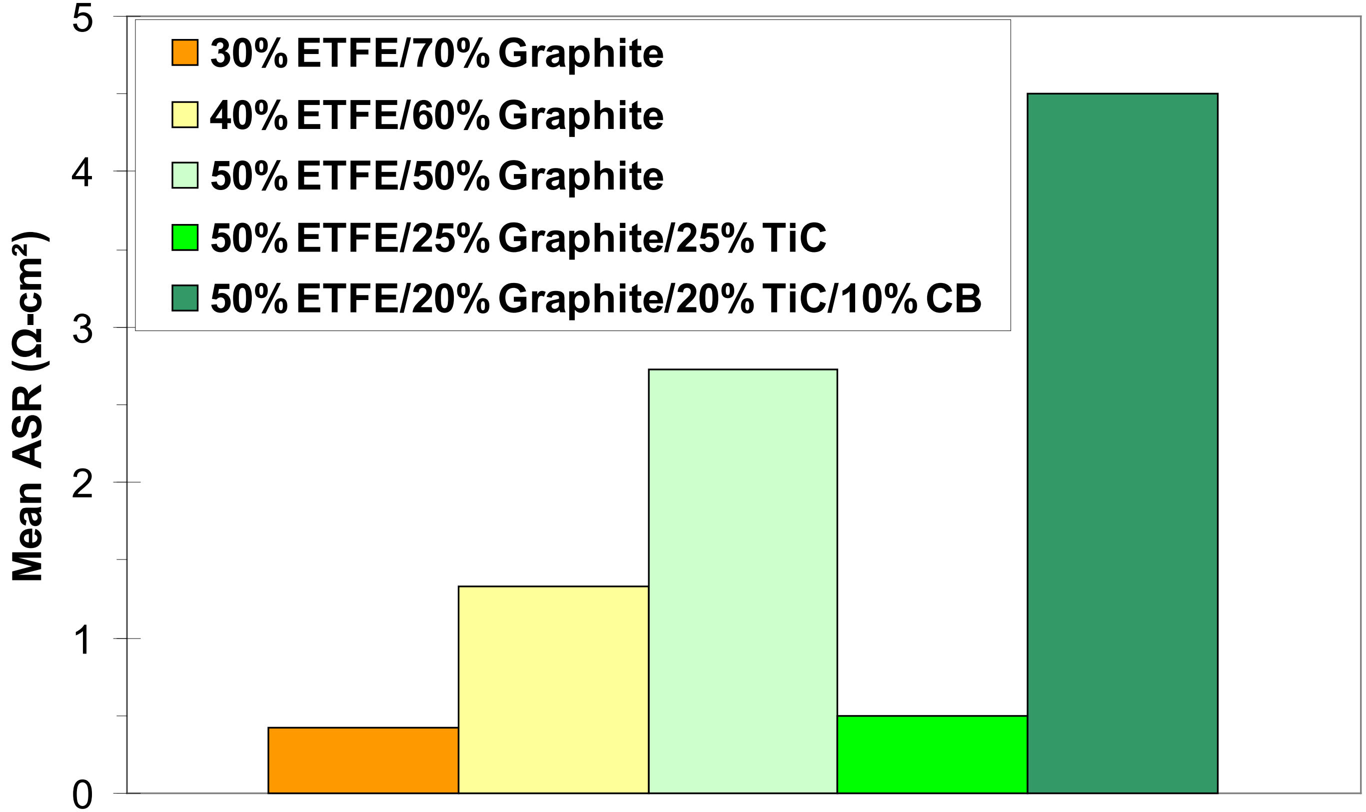


$$ASR_{sample} = (R_{total} - R_{baseline}) * area$$

- 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