(Metal) Bipolar Plate Testing

DOE 2017 Bipolar Plates Workshop

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DOE Fuel Cell Technologies Office Working Group Meetings and FC-PAD Meeting

May 2-4, Argonne National Laboratory

- Catalysis Working Group-Durability Working Group Meeting
 - ✓ Tuesday, May 2 to Wednesday, May 3
 - ✓ Open Meeting
 - ✓ Topics: PGM-free catalyst protocols and Pt alloy catalyst activity, performance and durability

• Durability Working Group-Transport Modeling Working Group

- ✓ Wednesday, May 3, afternoon to Thursday, May 4, mid-day
- ✓ Open Meeting
- ✓ Topics
 - Characterization of catalyst-ionomer interface (needs, current status, and limitations)
 - Information and tools needed for modeling at the macro-, micro-, molecular scales
 - Non-traditional diagnostics/tools

• FC-PAD Meeting

- ✓ Thursday, May 4, afternoon
- ✓ National laboratory and FOA project team members only

https://energy.gov/eere/fuelcells/fuel-cell-technologies-office-keyactivities#workgroups.



Bipolar Plate Targets + Protocols

Table 3.4.8 Technical Targets: Bipolar Plates for Transportation Applications				
Characteristic	Units	2015 Status	2020 Targets	
Cost ^a	\$ / kW _{net}	7 ^b	3	
Plate weight	kg / kW _{net}	<0.4 ^c	0.4	
Plate H ₂ permeation coefficient ^d	Std cm ³ /(sec cm ² Pa) @ 80°C, 3 atm 100% RH	O°	<1.3 x 10 ^{-14,f}	
Corrosion, anode ^g	μ A / cm²	No active peak ^h	<1 and no active peak	
Corrosion, cathode ⁱ	μA / cm²	<0.1 ^c	<1	
Electrical conductivity	S/cm	>100 ^j	>100	
Areal specific resistance ^k	ohm cm ²	0.006 ^h	<0.01	
Flexural strength ^l	MPa	>34 (carbon plate) ^m	>25	
Forming elongation ⁿ	%	20-40°	40	

^a Costs projected to high volume production (500,000 80 kW systems per year), assuming MEA meets performance target of 1,000 mW/cm².

- ^b Cost when producing sufficient plates for 500,000 systems per year. DOE Hydrogen and Fuel Cells Program Record 15015, "Fuel Cell System Cost—2015." http://www.hydrogen.energy.gov/program_records.html.
- ^c C.H. Wang (Treadstone), "Low-cost PEM Fuel Cell Metal Bipolar Plates," 2012 Annual Progress Report, http://www.hydrogen.energy.gov/pdfs/progress12/v h 1 wang 2012.pdf.
- ^d Per the standard gas transport test (ASTM D1434).
- ^e C.H. Wang (Treadstone), private communication, October 2014.
- f Blunk, et al, J. Power Sources 159 (2006) 533-542.
- ^g pH 3 0.1ppm HF, 80°C, peak active current <1x10⁻⁶ A/cm² (potentiodynamic test at 0.1 mV/s, -0.4V to +0.6V (Ag/AgC1)), deaerated with Ar purge.
- ^h Kumar, M. Ricketts, and S. Hirano, "Ex-situ evaluation of nanometer range gold coating on stainless steel substrate for automotive polymer electrolyte membrane fuel cell bipolar plate," Journal of Power Sources 195 (2010): 1401–1407, September 2009.
- ⁱ pH 3 0.1ppm HF, 80°C, passive current <5x10⁻⁸ A/cm² (potentiostatic test at +0.6V (Ag/AgCl) for >24h, aerated solution.
- ^j O. Adrianowycz (GrafTech), "Next Generation Bipolar Plates for Automotive PEM Fuel Cells," 2009 Annual Progress Report, http://www.hydrogen.energy.gov/pdfs/progress09/v_g_2_adrianowycz.pdf.
- ^k Includes interfacial contact resistance (on as received and after potentiostatic test) measured both sides per Wang, *et al.* J. Power Sources 115 (2003) 243–251 at 200 psi (138 N/cm²).
- ¹ ASTM-D 790-10 Standard Test Method for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials.
- ^m D. Haack et al. (Porvair), "Carbon-Carbon Bipolar Plates," 2007 Annual Progress Report, http://www.hydrogen.energy.gov/pdfs/progress07/v b 3 haack.pdf.
- ⁿ Per ASTM E8M-01 Standard Test Methods for Tension Testing of Metallic Materials, or demonstrate ability to stamp generic channel design with width, depth, and radius.
- ^o M. Brady et al. (Oak Ridge National Laboratory), "Nitrided Metallic Bipolar Plates," 2010 Annual Progress Report, <u>http://www.hydrogen.energy.gov/pdfs/progress10/v_1_1_brady.pdf</u>.

Corrosion Testing Protocol Variations

^g (Anode) pH 3, 0.1 ppm HF, 80°C, peak active current <1×10⁻⁶ A/cm² (potentiodynamic test at 0.1 mV/s, -0.4V to +0.6 V (Ag/AgCl)), de-aerated with Ar purge.
i (Cathode) pH 3, 0.1 ppm HF, 80°C, passive current <5×10⁻⁸ A/cm² (potentiostatic test at +0.6 V (Ag/AgCl)), for ≥24h, aerated solution.

NREL protocol

- 1M sulfuric + 2ppm F- at 70C
- Target current densities are roughly < 1 x 10-5 A/cm²
- De-aeration with Argon.

ORNL protocol

- Ar/H₂ or H₂ gases to get more controlled reducing conditions.
- Anode: pH 3, 0.1 ppm HF, 80°C peak active current < 1 x 10-6 A/cm2 (potentiodynamic test at 0.1 mV/s, -0.4 V to +0.6 V [Ag/AgCI], de-aerated with Ar)
- Cathode #1: pH 3, 0.1 ppm HF, 80°C passive current < 5 x 10-8 A/cm2 (potentiostatic test at + 0.6 V (Ag/AgCl) for at least 24 hrs, aerated solution)
- Cathode #2: pH 3, 80°C, passive current stable or decreasing (potentiostatic test at +1.6 V (NHE) for at least 6 hours, aerated solution)

LANL protocol(s)

- Anodic polarization curves, pH 1 3, 0.1 ppm HF, T= 25
- Simultaneous anode/cathode corrosion, electrolyte 3 ppm HF, bipolar configuration
- Additionally, corrosion cell putting plate in contact with PEM

Test condition variables

- Potential (potentiodynamic, potentiostatic, potential limits)
- Temperatures
- Concentration of sulfuric acid
- Concentration of F-



Metal Bipolar Plate Anodic Polarization Corrosion Results

- Different metals (316L S.S., NiCr, Hastelloy)
- Temperature effect
- Fluoride anion content effect



50mV below the Open Circuit Potential (Free Corrosion Potential) and scan in the positive direction at 0.1 mV/s 1.5V vs. SHE.

- Temperature increases corrosion rate
 - Decreases Free Corrosion Potential (OCV)
- Flouride ions show weak increase corrosion current
- Higher corrosion with temperature



Corrosion Testing of Metal Bipolar Plates



• Potentiometric measurements to rapidly characterize dissolution behavior

- Mirror environment seen by bipolar plate material in a PEM cell
- Potentiometric studies performed at a pH of 3
- Ionomer membrane is replaced with a 0.001 N H₂SO₄ solution containing 2 ppm F-.
- ELAT electrode (0.5 mg Pt/cm2, 20% Pt on C), establishes the electrochemical potential
- Electrical potential between components is recorded to monitor oxide growth.
- Hydrogen and air are supplied to the anode and cathode faces, respectively.

U.S. Patent # 6,454,922 Wiesbrod (2002)

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Contact Resistance

- Measure contact resistance between metal plate and GDL material
 - Compaction force
 - 150 to 200 N/cm² c
 - bipolar plate material/carbon paper interface
 - (one or two?)
 - Target: 1 face value of 0.01 to 0.02 ohm-cm² at 150 N/cm²



Dionissios D. Papadias, Rajesh K. Ahluwalia, Jeffery K. Thomson, Harry M. Meyer III, Michael P. Brady, Heli Wang, John A. Turner, Rangachary Mukundan, Rod Borup, **Degradation of SS316L bipolar plates in simulated fuel cell environment: Corrosion rate, barrier film formation kinetics and contact resistance,** Journal of Power Sources, Volume 273, 2015, 1237 - 1249

Interfacial Resistance after Polarization



Interfacial contact resistances (Experimental and Modeling) of 316L and Nitrided G35 at different compaction pressures and exposure potentials.



- Leachant / Corrosion Testing ---- COMPOSITE BIPOLAR PLATES

 Various additives often contain metal ion containing compounds. Leaching of the metal ions into the fuel cell stack and/or membrane is of concern.

• Molded composite samples are placed in individual bottles containing 200 ml of dilute sulfuric acid (pH = 2 or 6) and a strip of Nafion membrane.

• Gravimetric testing is used to evaluate "corrosion" and XRF testing of solutions and Nafion membranes is used to evaluate leachants.

•A few membranes were pulled and analyzed after 500 h, preliminary XRF results indicate that:

- All membrane samples have < μ M amounts of Ca and Fe.
- No Co detected in samples with Co napthenate.
- Ca levels in samples w/ Ca stearate is no higher than w/o.
- The + 99.9% pure graphite is the primary source of Fe and Ca!





ASTM D1434

Standard Test Method for Determining Gas Permeability Characteristics of Plastic Film and Sheeting

E8/E8M – 16a Standard Test Methods for Tension Testing of Metallic Materials

D790 - 15

Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials

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Drive Cycle Testing



- a. The following parameters are constant throughout the test: anode inlet composition of $80\% H_2 / 20\% N_2$ (excluding water vapor), cathode inlet composition of $21\% O_2 / 79\% N_2$ (excluding water vapor), anode and cathode outlet pressures of 101.3 kPa_{abs}, cell/stack control temperature of 80° C, and set point transition time of 0 s.
- b. Drive cycle testing only reflects degradation losses associated with wet and dry cyclic operation. Other relevant stressors, including startup/shutdown and freeze operation, are not included in this test.
- c. A protocol such as the one in Table A9 should be used to recover reversible losses at least once every 24 h.
- d. The 5 minute hold in step RH20 is intended to represent a system idle point.

Optical Pictures of Metal Hardware

After Testing

(Anode Plate) **Before Testing** . . Outlet

Inlet

After Testing (Cathode Plate)



•After testing and disassembly visible changes:

- Anode Plate: bottom (outlet) of anode plate shows significant change
- Cathode Plate: sporadic discoloration on lands



Previous work by LANL with identical flowfield geometry under similar operating conditions (100% RH, H2/Air co-flow with outlets at hardware bottom) show liquid water in the hardware flowfield, remarkably similar to the corrosion pattern observed in the Treadstone test.

In situ Metal Bipolar Plate Fuel Cell Durability Results



No Visible Corrosion

Nitrided Haselloy plates

- No increase in MEA Metal Cations
- MEA post-characterization shows lower cation content in MEA after use compared with initial



 Increase in plate contact resistance observed at low contact force

Torque (lb-in)

Voltage vs. current plots for various compressions of BC25 GDLs between

Hastelloy endplates.

- Partially reversible
- High contact force inverse



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Tested Metal Bipolar-Plates

Discoloration where spot-welding occurred



- Testing created two areas of discoloration
 - Circles in channels where spot-welding was conducted (white-ish)
 - Darker discoloration in channels sporadically
- Changes in surface coloration due to small TiOx thickness changes
 - TIOx essentially insoluable; have not seen cationic contamination of MEAs due to Ti

Revised Drive Cycle Protocol: Shut-Down/Start-Up



-1

0

0.2

0.4

0.6s

(measured residence time)

0.6

Time (s

0.8

1

1.2

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- Exposure time short, of < 1 sec
- Important for Cathode Catalyst Layer Carbon corrosion
- For bipolar plates?

Summary Protocols: Ex situ and In situ Testing

- Ex situ testing protocols
 - Potentiodynamic (Anodic Polarization) and Potentiostatic
 - Anodic Polarization
 - Start ~ 0.1 V negative of free corrosion, to $\sim 1.2 V$
 - Anode Plate: pH 3, 0.1 ppm HF, 80°C
 - potentiodynamic test at 0.1 mV/s, \sim -0.2V to +0.8 V de-aerated with Ar purge.
 - Cathode Plate: pH 3, 0.1 ppm HF, 80°C
 - − potentiostatic test at ~ +0.8 V, for \geq 24h, aerated solution

In situ testing protocol

- Fuel Cell Drive Cycle Test
 - Over-saturation RH level
 - Potential cycling used to enhance corrosion rate of metal
 - Hydrogen worse for passivation due to reduction of oxide layer
 - Testing to-date does not include:
 - Shut-down/Start-Up
 - Free corrosion (extended time at off conditions)
 - » may/may not matter depending upon liquid water removal

Supplemental

Metal Plate Testing Results

Degradation

- Metal Corrosion
 - More severe on anode plate
 - Lower passivation due to hydrogen and lower potential, high water content
- Contact Resistance increase
 - Surface Oxidation
 - More severe on cathode plate (expected)
- Membrane Resistance increase
 - Metal cations must migrate into MEA/Membrane for degradation
- Visible discoloration changes may not correlate to performance losses
- With good corrosion resistant metal plates, LANL observed a negative cation flux into membrane/MEA from metal plate
 - (i.e. initial MEA cation concentration was measureable; final was below detection limits)

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Local currents during Shut-down / Start-up Transients

Measure carbon corrosion by linear series segments and CO₂ by NDIR







20 linear segments in series



Recent Reviewer Comments from Borup Durability Related Projects

- 2014 Comments:
 - Fe from plate initiating PEM degradation or F- causing plate corrosion
 - Fruitful work to be done on bipolar plate durability studies... lower grade metals such as ferritics
- There are not well-defined tests for bipolar plates. Work exploring the failure modes and stressors for a range of bipolar plate coatings could be beneficial. What conditions lead to bipolar plate corrosion, discoloration, etc.? can focus on developing bipolar plate testing protocols?

Metal Bipolar Plates – Research Needs

Work on life prediction strategy of coatings

- Consider and incorporate more aspects of corrosion; such as potential holds and potential cycles, crevice corrosion, and impact of calendar life (prolonged off condition)
- AST development to support life prediction model

Potential hold studies

- Define the limits of the candidate materials
- Emphasis on key substrates as a baseline
- Map out corrosion as function of pH, temperature, and potential
- Impact of welding treatments on base materials and surface coatings as it relates to corrosion stability
- Interactions between plate corrosion and membrane degradation
 - Coupling effects that accelerate transfer leaks and corrosion
- Assessment of existing models on plate corrosion
 - Corrosion mechanisms
 - Transport of metal species in fuel cell
 - Rate of accumulation of metal species in MEA materials
 - Gap analysis/validation and public dissemination of DOE models

Compatibility with Hydrogen atmosphere for a range of conditions

Experimental

Electrolyte Preparation

1.00 mL of stock 0.01% HF (w/v) is added to 999.00 mL of 18.0 M Ω deionized water resulting in a 0.1ppm fluoride solution. The pH of the solution is adjusted to 3.00 by dropwise addition of 1M sulfuric acid with constant stirring. A fresh electrolyte was prepared for each test.

Sample Preparation

A stainless steel clip is attached to the metal sample which is approximately 2cm x 2cm in size. Two coats of glyptal enamel are painted over the entire surface and clip with the exception a 1cmx1cm area on one face of the sample. The enamel is allowed to cure for 24 hours between coats and before the sample testing.

Electrochemical Cell Setup

The electrolyte is added to a closed, six port water-jacketed cell. Temperature of the electrolyte is maintained by an external heated water bath flowing at a constant rate. The temperature is monitored by a teflon coated type K thermocouple suspended into the electrolyte. The electrolyte is purged with compressed dry air (20% oxygen , 80% nitrogen) flowing through a glass frit throughout the entire run. A condenser with flowing chilled water (T=5°C) is attached to the cell. The counter electrode consists of a platinum flag (2cmx1cm) suspended in the solution with a platinum wire. The reference electrode is a saturated calomel electrode (SCE offset +0.224V vs. SHE) placed in a salt bridge filled with electrolyte. The working electrode is suspended into the solution with a stainless steel rod such that the exposed sample face is below the electrolyte surface level and no part of the unpainted metal clip or rod come into contact with the electrolyte. The working electrode is allowed to equilibrate at temperature (either 40°C or 80°C) in the aerated electrolyte for one hour.

Polarization Parameters

A Princeton Applied Research model 273A potentiostat was used for all tests. The parameters were set to start the scan at 50mV below the open circuit potential and scan in the positive direction at 0.1 mV/s to a maximum of 1.5V vs. SHE. The instrument does not initiate the scan until the drift stability of the open circuit potential drops below 0.5mV/s. In most cases the scan would initiate within 5 minutes after activating the program.