Corrosion Resistant Metallic Components for Electrochemical Devices

Fraunhofer ISE, Freiburg, Germany

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First International Workshop
Durability and Degradation Issues in PEM Electrolysis Cells and Its Components

TreadStone Technologies, Inc.
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USA

TreadStone's Background and Mission

Corporate Background

- *TreadStone is a small business technology spin-out of SRI-Sarnoff Corporation in March 2006*
- *Focused on the technology development for electrochemical power systems*
- *The core metal corrosion protection technology has been developed for over 8 years. The US Patent (US 7,309,540) was issued on 2007.*
- *It has been evaluated by various clients for various systems.*

Corporate Mission

Achieving continuous growth in profits, revenue and net worth through the commercialization of new technologies for the energy market.

Metal Plate Technology Development at TreadStone

SARNOFF Corporation — a subsidiary of SRI International

TreadStone Technologies, Inc.

2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013

2003–2006

- Plate Design Invention
- Demonstration using Titanium w/gold
- Funded by:
  - Sarnoff
  - A DoD Project

2006–2009

- Processing Invention
- Demonstration using SS w/gold
- Funded by:
  - Private Investors
  - NJ CST

2009–2011

- Demonstration in PEM fuel cells
- Commercial sales since ‘09
- Funded by:
  - Private Investors
  - DOE EERE
  - DoD SBIR

2011–

- Extend the application into electrolyzer and other. devices.
- Used in NASA’s new generation fuel cells
- Funded by:
  - Private Investors
  - ARPA-E, DOE
  - DoD SBIR

Technical Challenge: Meet both corrosion resistant and surface electrical conductance requirements at low cost

Focused Market

Fuel Cell Market

Automotive

----Commercial Applications ----

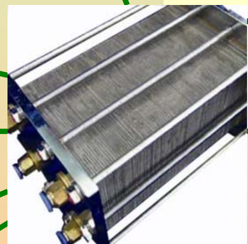
Back-up Power

Materials Handling

Combined Heat & Power

Long runtime & Short refueling time

Safe, low-emissions power



----- Military Applications -----

High Energy Density

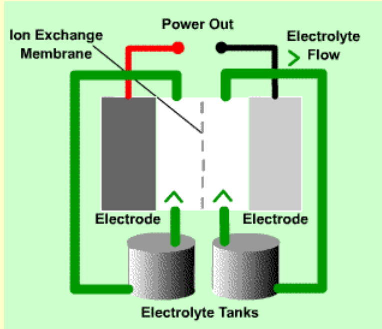
Shipboard Power

UAV & UUV

Specialty Applications - NASA

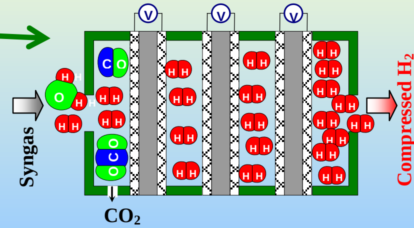
Energy Storage Applications

Flow Batteries



High energy efficiency and independence

Electrochemical Compression



Long lived – low maintenance power

Electrolyzers

Hydrogen Generation & Delivery

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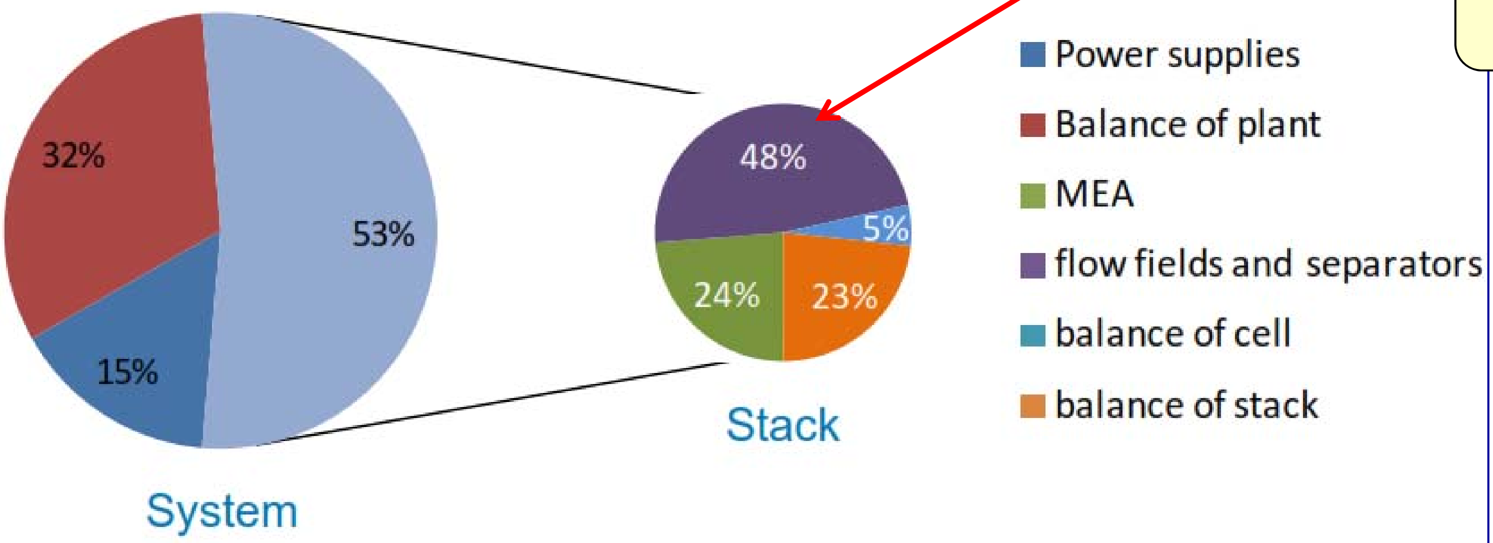
PEM Electrolysis System Cost Break-down

Relevance
Overall Cost of Hydrogen

- Cell stack largest contributor to system cost
  - Flowfields, separators and MEAs drive stack cost

Cost Reduction:
- Cell/Stack Design
- <u>Plate processing technology</u>

TreadStone's focus



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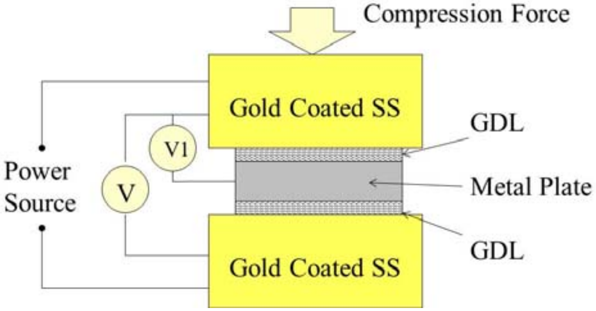
Proton ENERGY SYSTEMS

Metal Plate Performance Evaluation Methods

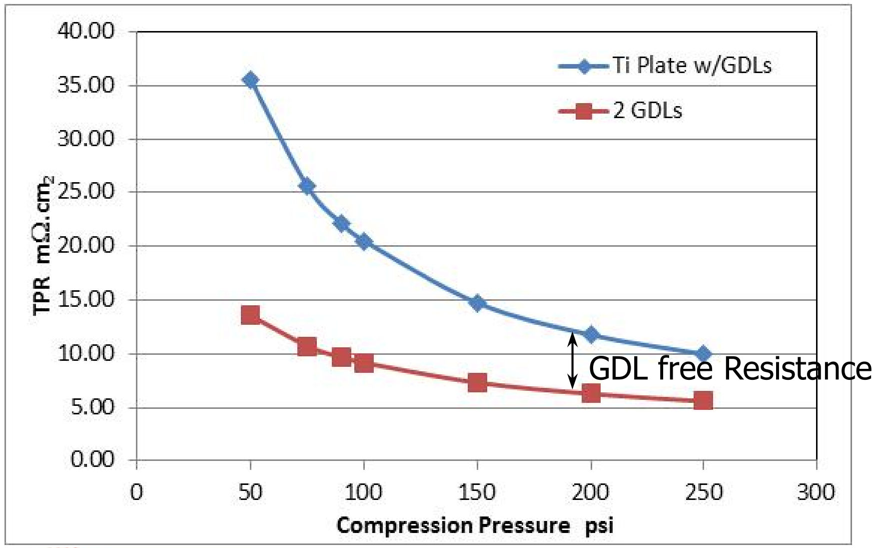
1. Electrical Resistance

Before and after corrosion tests

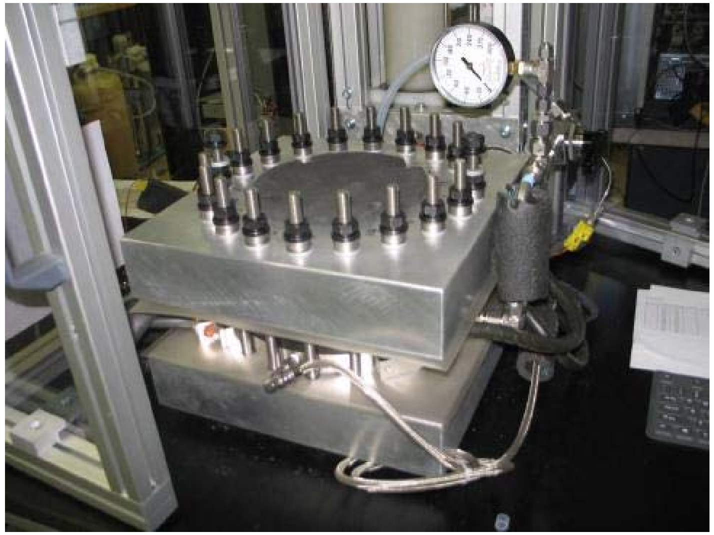


Through Plate Resistance (TPR) = V/I

Contact Resistance (CR) = V_1/I



2. Cell/Stack Performance



3. Hydrogen Absorption

Hydrogen embrittlement failure if H_2 >8000 ppm in Ti

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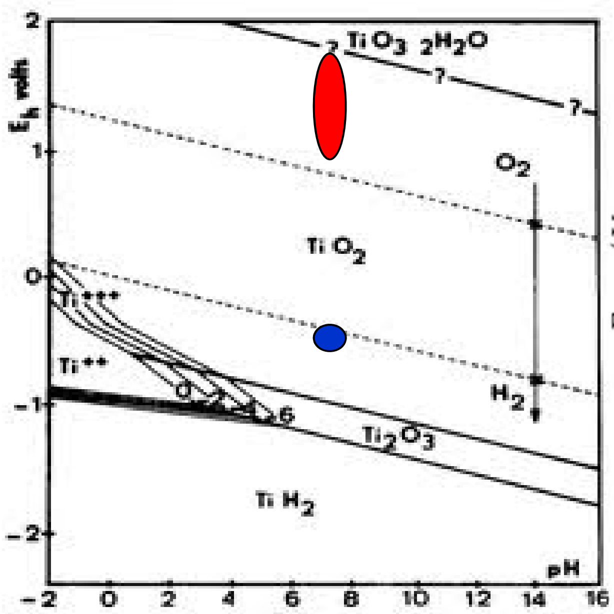
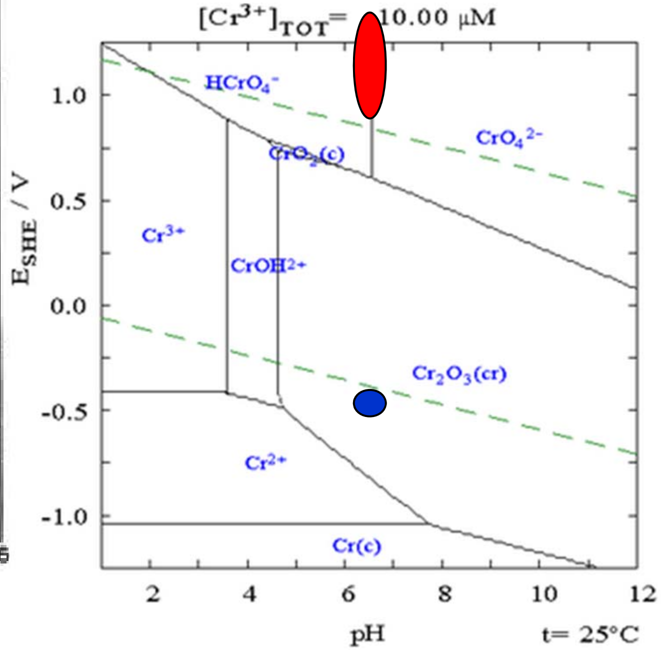
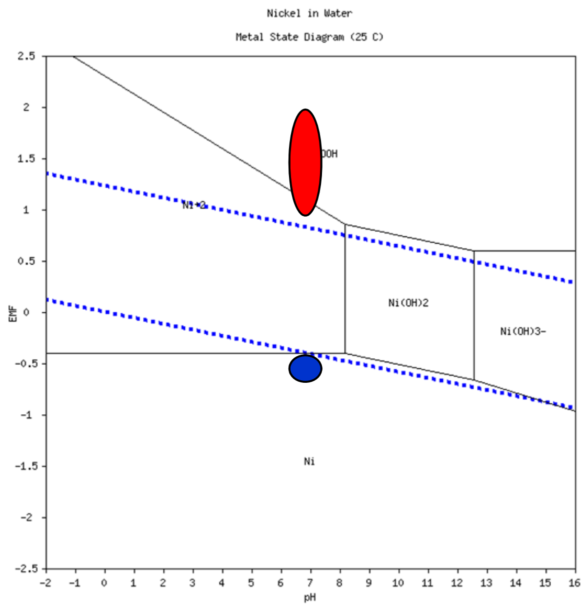
Substrate Material Selection for PEM Electrolysis

Pourbaix Diagram







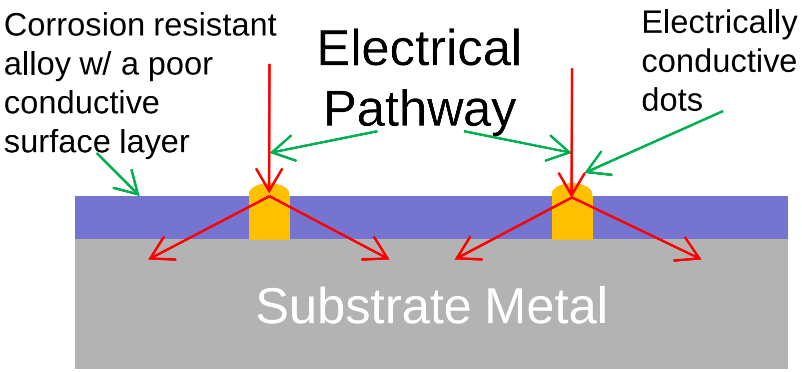
PEM Electrolysis

- Anode Working Condition (red marker)
- Cathode Working Condition (blue marker)

Challenge:
High electrical resistance of TiO_2 surface layer

- Ti has desired corrosion resistant, thanks to the dense TiO_2 surface layer.
- Ni and stainless steel is not stable for PEM electrolysis

TreadStone' Metal Plate Technologies



Design Feature:

1. Using a small amount of electrically conductive and corrosion resistant material to cover a small portion of the substrate surface in the form of isolated vias (dots).
   - Low cost
2. Using non-conductive (or poor conductive) material to cover the rest of the substrate surface and separate conductive vias.
   - Eliminate galvanic corrosion
   - Easy processing

Electrical Resistivity

Graphite:	1375 μΩ.cm
Gold:	2.2 μΩ.cm
Silver:	1.6 μΩ.cm

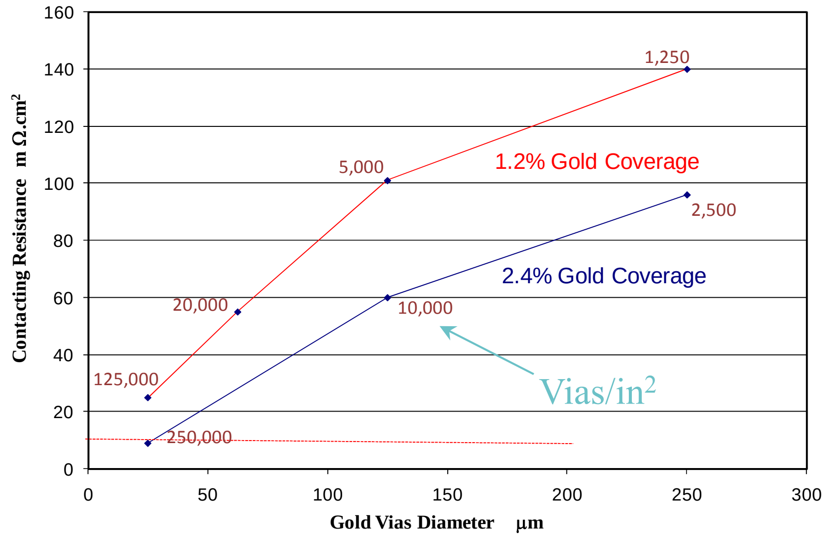
Highly conductive small vias can ensure the sufficient low electrical contact resistance of the metal plates for electrochemical applications

Proof of the Concept Experiments

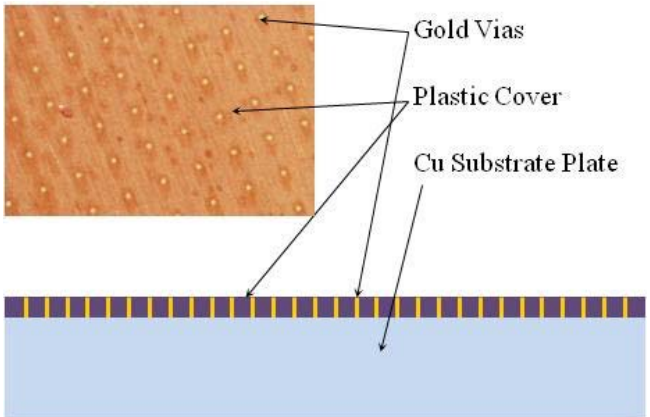
Experiment Procedure

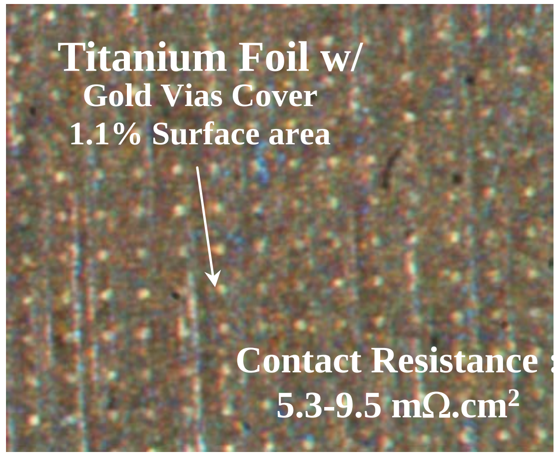
1. Plate samples were prepared using Cu plate covered with plastic (photoresist) film.
2. Gold vias were processed using photolithography and electrical plating.
3. The gold vias size and distribution density were precisely controlled by the photolithography process.
4. Contact resistance of GDL with plates having various gold vias were measured

Contact Resistance of GDL with the Cu/Plastic Film/Gold vias Plate

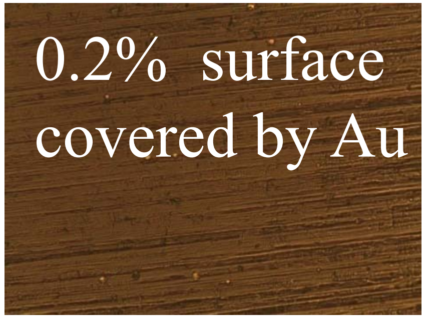


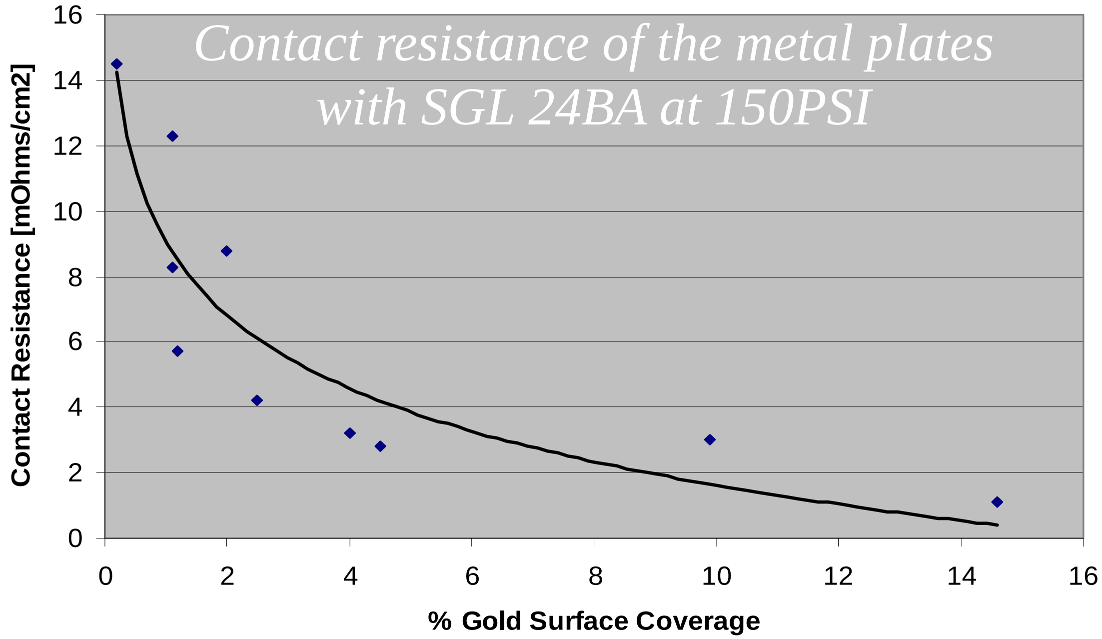
Sample Picture and the Schematic Drawing

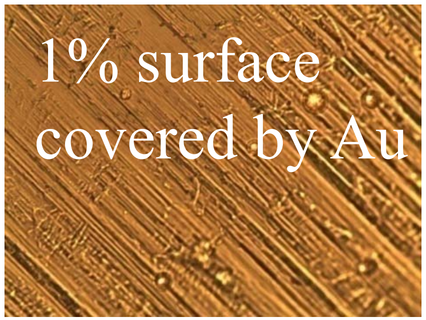


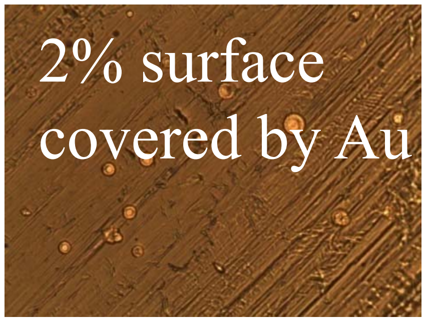


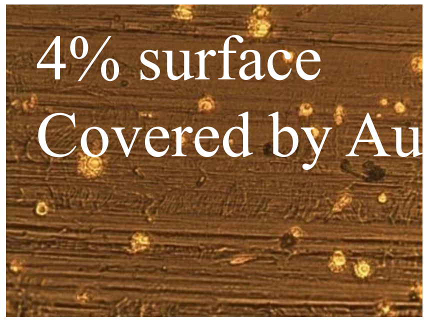
Electrical Contact Resistance vs Gold Coverage











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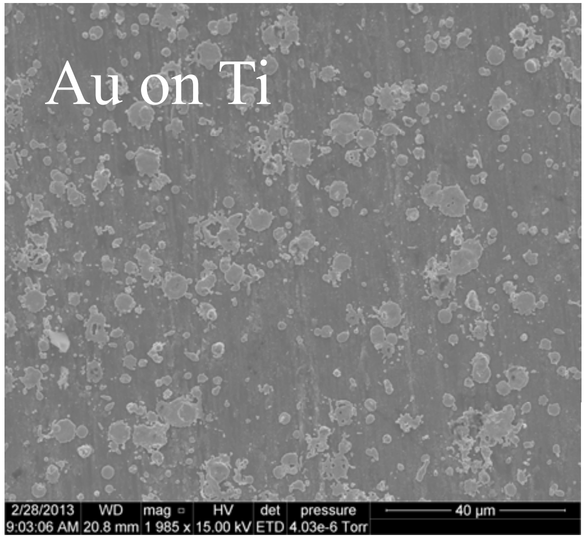
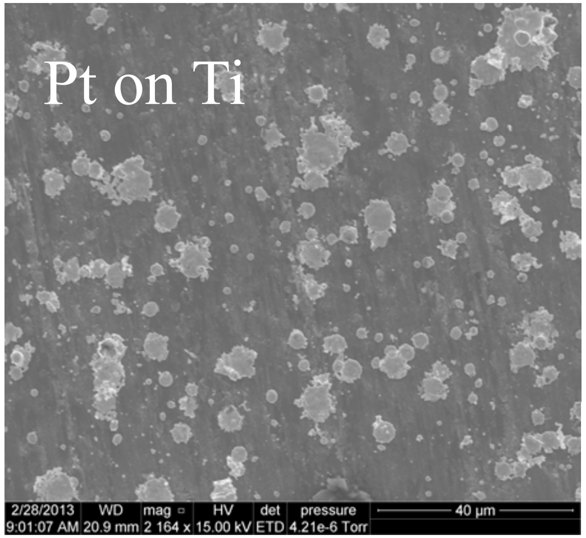
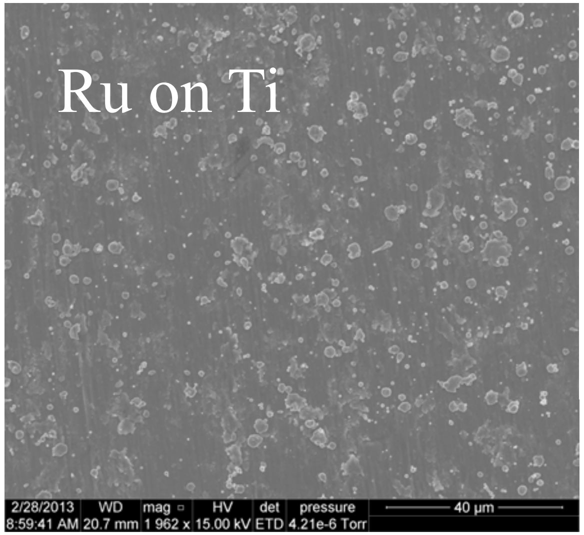
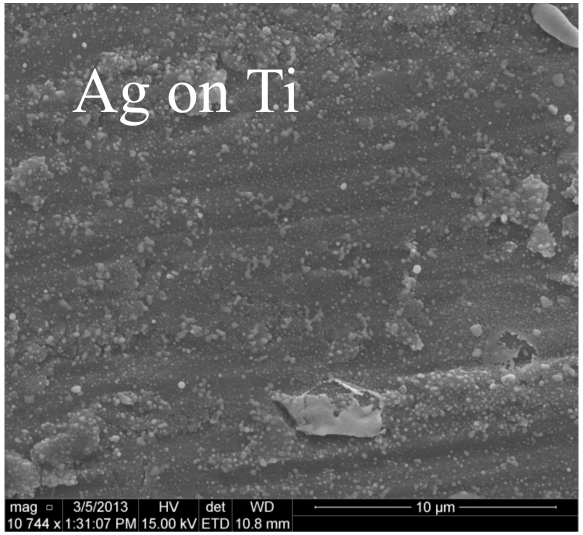
SEM Pictures of Precious Metal on Ti Substrate









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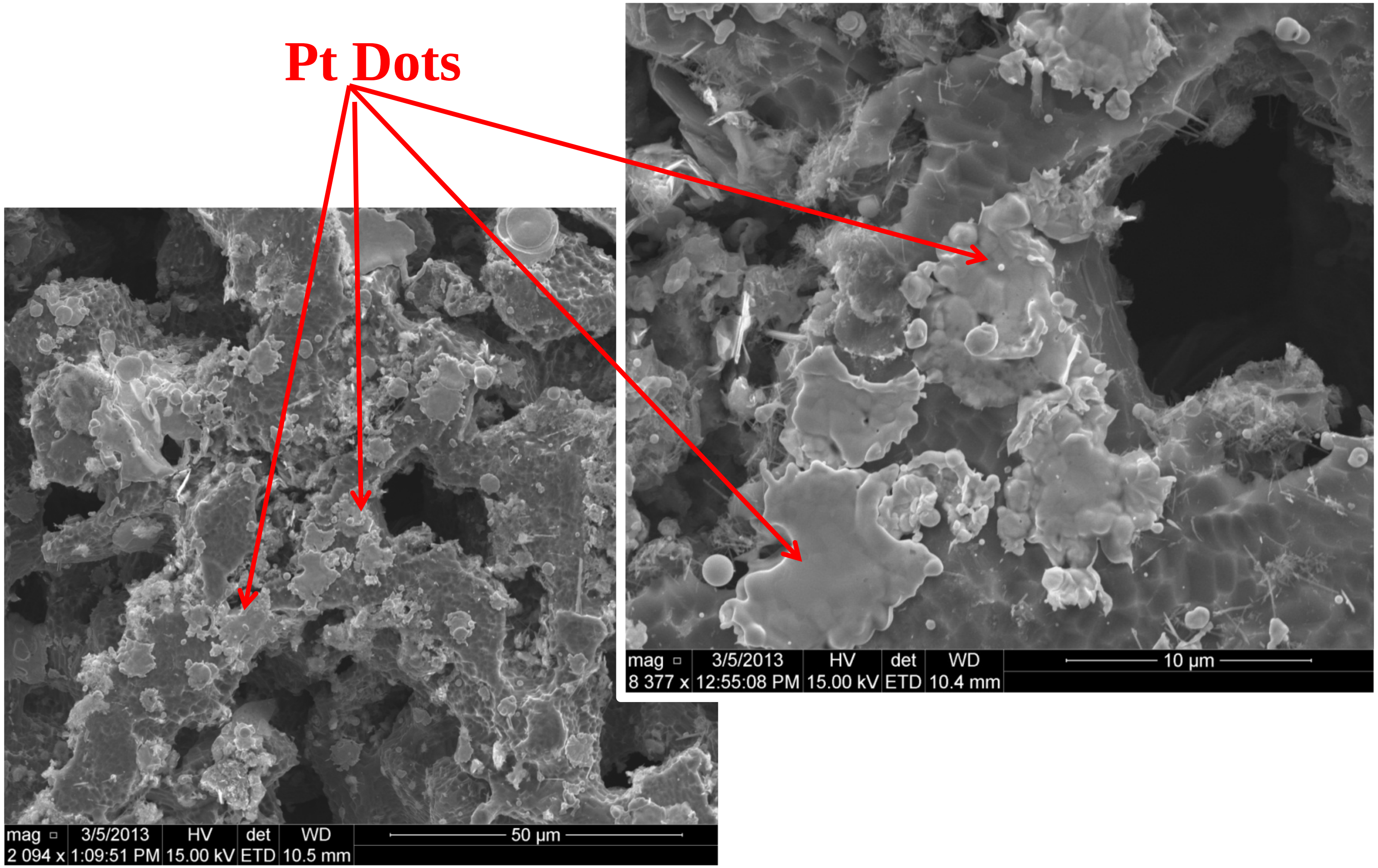
SEM Pictures of Pt on Porous Ti Plate



Long term Durability Test in PEM Electrolyzers

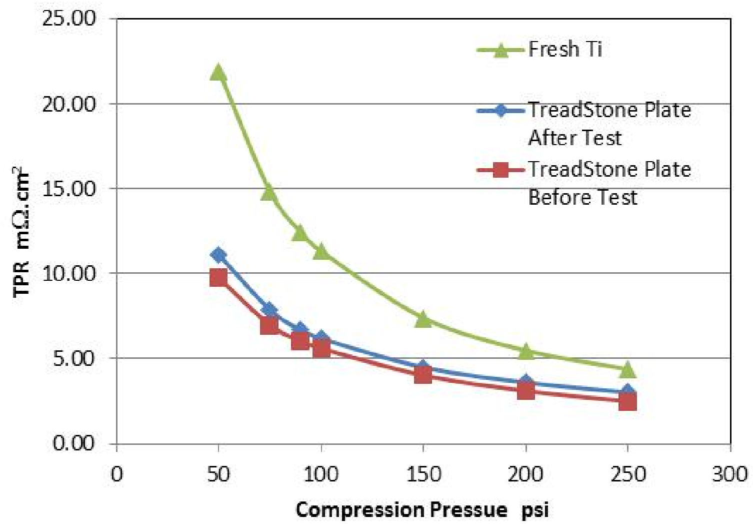
Under Stable Operation Conditions (1.8-2.0 V/cell)

Bipolar Separator Plate	H_2 pressure (psi)	Time (Hours)	H_2 uptake (ppm)
TreadStone Ti Bipolar Plate (120 cm²)*	2400	1000	51
TreadStone Ti Bipolar Plate (250 cm²)	230	5365	55
Zr/Ti (160 cm²)	230	500	140
Dual Layer Ti (160 cm²)	230	500	1105
Ti (as received)	-	0	≈ 60

Under Accelerate Testing Condition for 1000 hrs (high voltage, pressure cycles)

Bipolar Separator Plate	H_2 uptake (ppm)
TreadStone Ti Bipolar Plate (160 cm²)	160
Dual Layer Ti (160 cm²)	> 2000

* High pressure stack test was done at Proton Onsite.
Others were tested at Giner
Ti plate thickness: 0.1-0.15 mm



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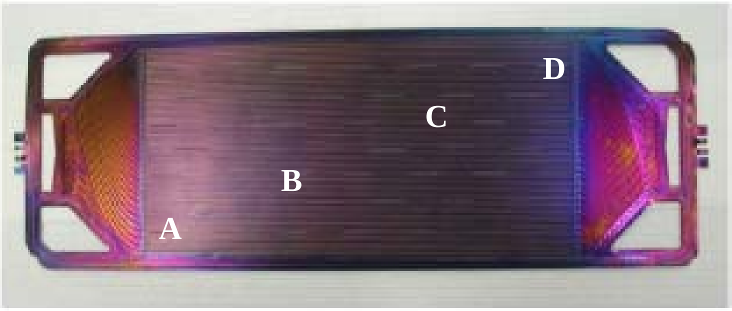
TreadStone Metal Plates for PEM Fuel Cells

Attribute	Metric	Unit	2015 DOE Target	Ford Data on Au-Dots
Corrosion anode	**Current density at active peak in CV**	μA/cm²	<1	No active peak
Corrosion cathode	**Current density at 0.8 V_{NHE} in potentiostatic expt.**	μA/cm²	<1	~0.1
Area Specific Resistance	**ASR (measured through plane) at 6 bar contact pressure** (includes both side surface; doesn't include carbon paper contribution)	mOhm.cm²	<20	8.70 (as-recd flat samples)
Electrical Conductivity	**In-plane electrical conductivity (4-point probe)**	S/cm	>100	34 kS/cm
Formability	**% elongation** **(ASTM E8M-01)**	%	>40%	53(|| to RD*)/ 64 (⊥ to RD)
Weight	**Weight per unit net power** (80 kWnet system)	Kg/kW	<0.4	<0.30

*RD: Rolling Direction

Plate Resistance Consistency



As presented by Ford Motor Company at 2011 Fuel Cell Seminar, Orlando, FL . Nov. 1 2011

Processed 5 plates and measured TPV at 4 locations on each plate

Plate #	TPV mV (@ 1A/cm^2)				
	A	B	C	D	Average
#1	6.75	6.14	6.64	6.45	6.50
#2	5.36	6.25	6.95	6.60	6.29
#3	7.60	7.12	7.00	6.40	7.03
#4	7.00	6.40	6.00	7.40	6.70
#5	7.60	6.90	7.50	7.50	7.38

The process has met Ford's requirements

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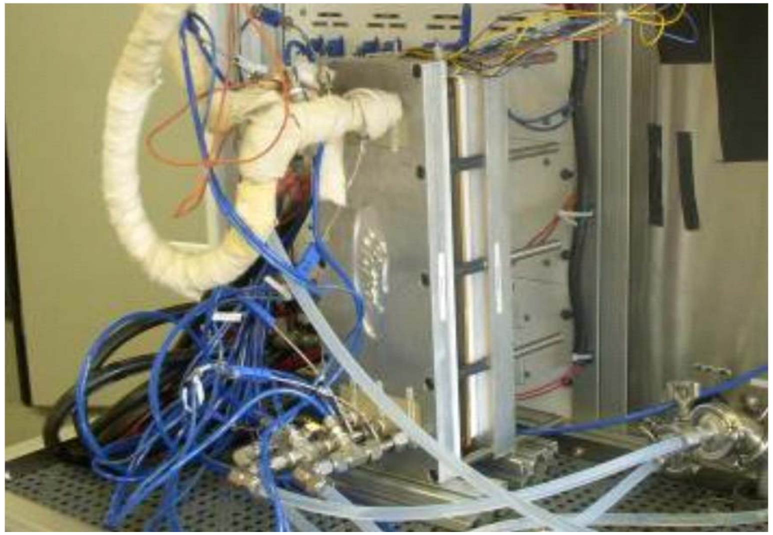
Short Stack in-situ Testing at Ford

- *TreadStone SS plates w/ Au dots were tested in-situ for durability at Ford Motor Company.*
- *Ford designed metallic bipolar plate w/SS316L as base substrate, 300 cm^2 active area. TreadStone applied the coating*
- *20-cell, 5 kW short stack test:*
  - *The stack is being tested for durability utilizing durability cycle (which includes FTP cycle along with others) mimicking real world driving conditions.*
  - *finished 1500 hrs test without degradation. Plan to finish 4000 hrs this year.*
  - *Took one plate out of the stack every 500 hours for post-test evaluation.*

Ford short stack with TreadStone metal bipolar plates



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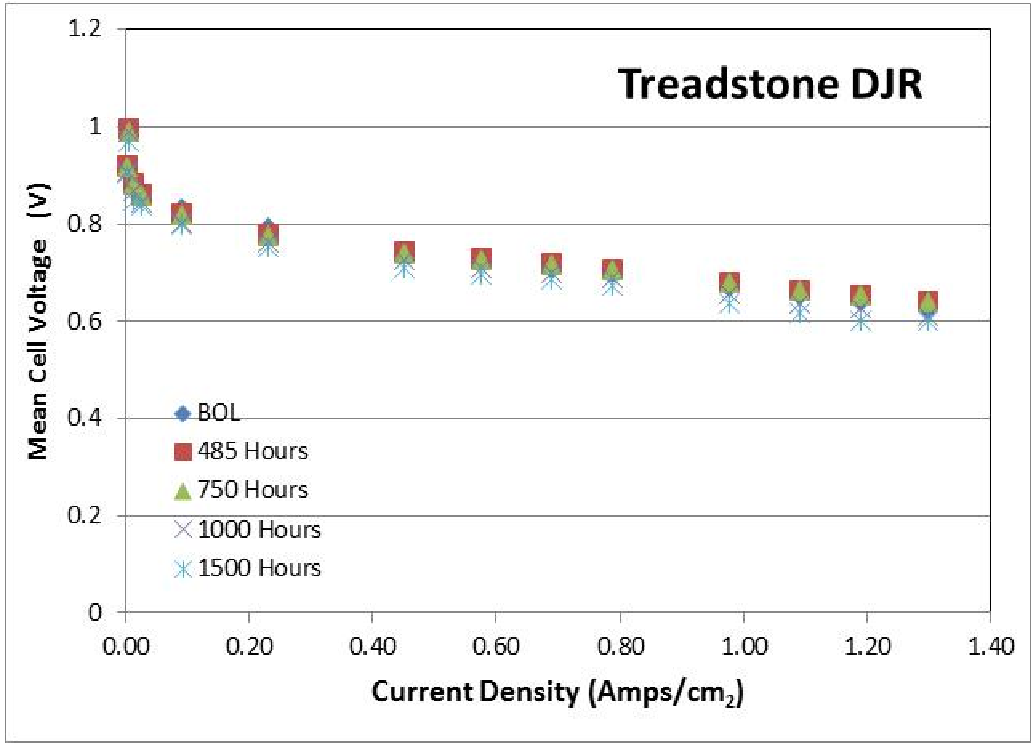
20-cell Stack Performance



TPR [mΩ.cm^2] before and after stack tests

BOL Plate #3	500 hrs Plate #18	1000 hrs Plate #19	1500 hrs Plate #20
8.52	5.90	7.21	5.90

Summary

- ***TreadStone's metal plate technology uses a unique design and processing technique for cost reduction, while meet metal plate's technical requirements (high corrosion resistant & low electrical resistance).***
- ***The technology has been demonstrated several thousand hours stable operation in PEM electrolyzer.***
- ***TreadStone's metal plate technology been demonstrated for low temperature PEM fuel cell applications***
- ***Further development is focused on the process optimization and using lower cost materials for fabrication cost reduction (supported by DOE).***
- ***The investigation of the technology for other electrochemical applications is under way.***
- ***Seeking partnerships to…***
  - ***Enhance commercialization activities***
  - ***Scale process to high volume production***