Corrosion Resistant Coating of Metal Bipolar Plates for PEM Fuel Cells

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Workshop on Research and Development Needs for Bipolar Plates for PEM Fuel Cell Technologies

Southfield, MI

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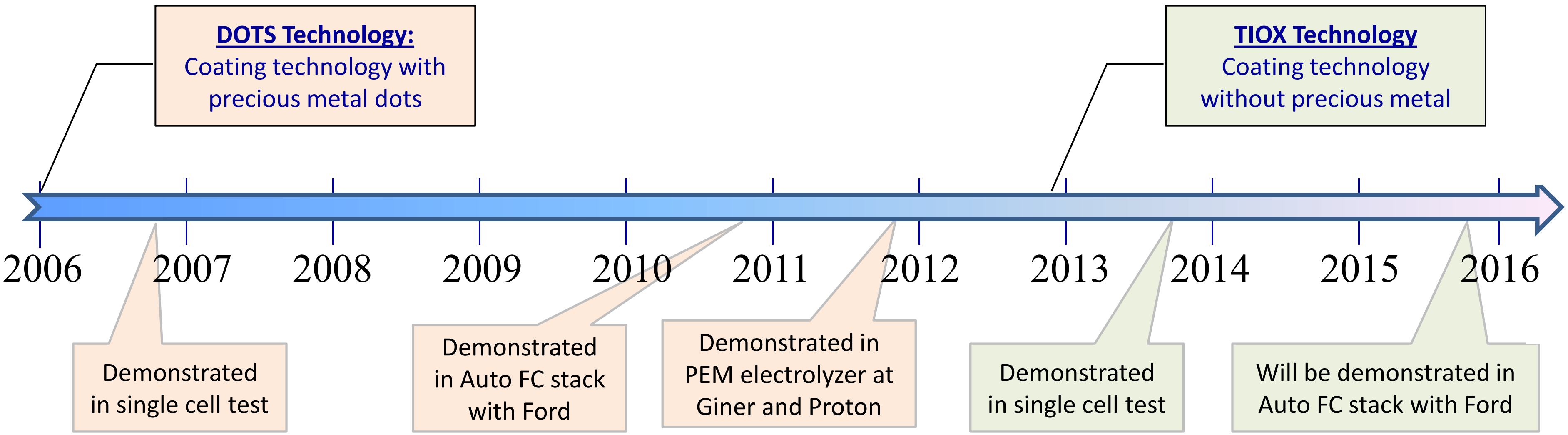
Metal Plate Technology Development at TreadStone



Coating with precious metals

- Exceptional stability and electrical conductivity.
- Focus is on precious metal usage reduction and adhesion of coating on substrate.
  - ✓ Reduce the precious metal coating thickness.
  - ✓ Reduce the surface coverage of precious metal on metal substrate.

Coating without precious metals

- Low material cost. Final cost is dominated by the coating processing cost.
- Challenges in long term durability, especially at high potential transit conditions.
  - ✓ Metal nitride is the most investigated coating. The challenge is the stability of the coating at stack transient operation conditions.
  - ✓ Graphite coating is used in some systems. A thick coating is needed to meet the long term (>5,000 hrs) operation requirement. The fabrication cost of the thick coating is an issue.
  - ✓ Conductive metal oxide is the more attractive approach for long term stability.

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Challenges to Metal Bipolar Plates

DOE's Performance Requirements for PEM Fuel Cell Bipolar Plates		
Characteristic	Units	2020 Targets
Cost	\$ / kW	<3
H2 permeation coefficient	Std $cm^3/(sec.cm^2\ Pa)$	<1.3 x 10–14
Corrosion, anode*	$\mu A / cm^2$	<1
Corrosion, cathode*	$\mu A / cm^2$	<1
Electrical conductivity	S / cm	>100
Areal specific resistance	Ohm-cm^2	0.01
Flexural strength	Mpa	>25
Forming elongation	%	40

Require:

1. Sufficient corrosion resistance in PEM fuel cell stack operation conditions
2. Low surface electrical contact resistance with GDL
3. Low cost.

* Standard test condition is in pH 3 H_2SO_4 + 0.1 ppm HF solution at 80^oC

- Potentiostatic test at 0.8V_{NHE} for 100 hours.
- Potentiodynamic test at 10 mV/min scan rate.

* The resistance requirement is at the end of life. The resistance at the beginning of the life should be further lower.

* The corrosion test condition at stack transient operation conditions is not defined by DOE. Each OEM has their own testing protocols.

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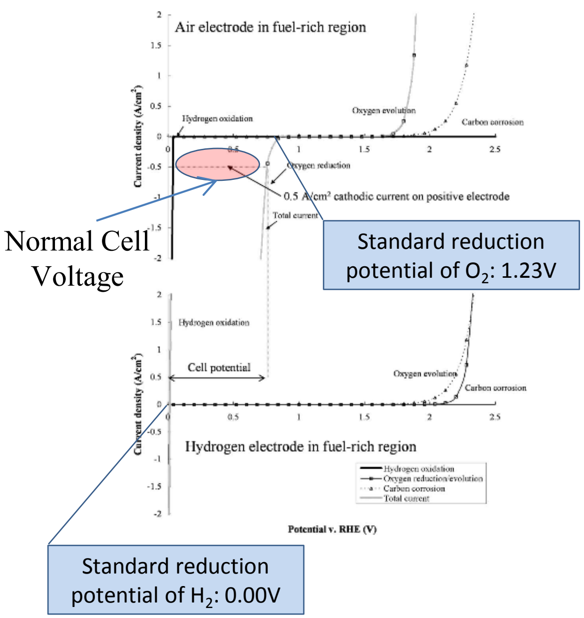
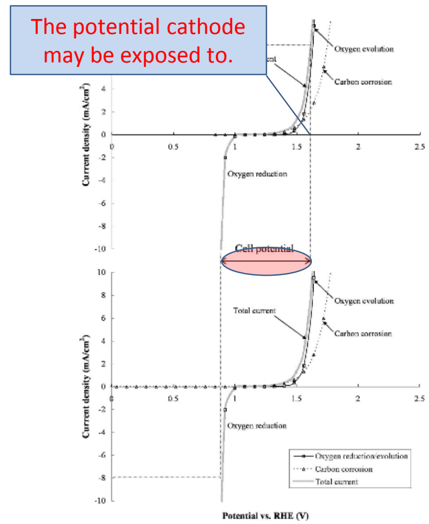
PEM Fuel Cell Operation Environment

Normal Operation Condition



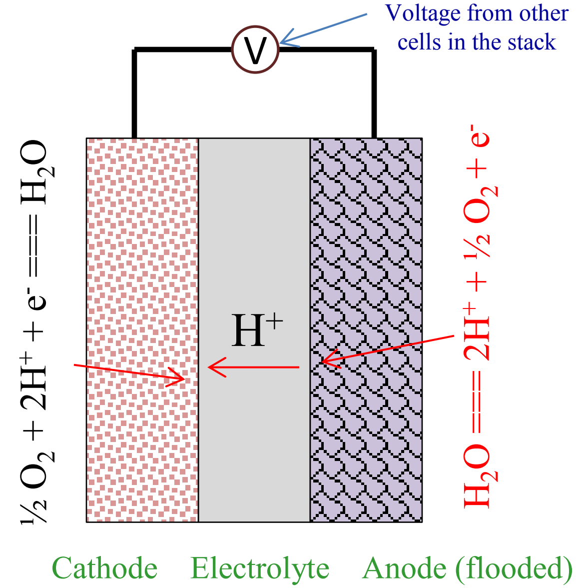
Transient Operation Conditions

During stack start-up and shut-down



- Cathode side may be pushed to the high potential of oxygen evolution

At flooded anode of individual cells in a stack



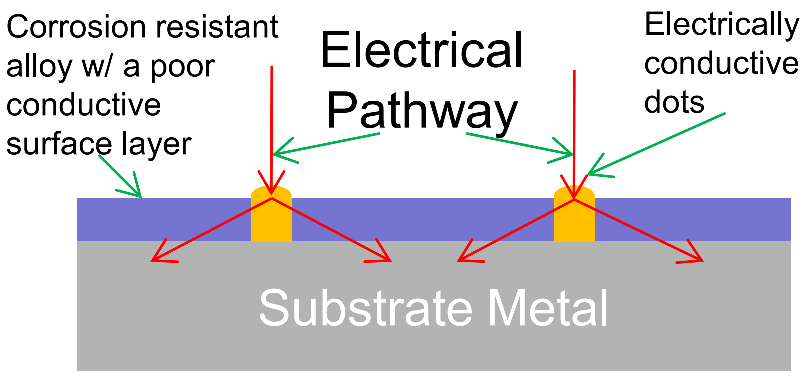
- No hydrogen to generate proton in flooded anode.
- Power from other cells in the stack forces the proton generation by water electrolysis reaction.
- High potential in anode for water electrolysis reactions.

J. P. Meyers, R. M. Darling, JECS., 153, A1432-A1442 (2006)

- The corrosion of fuel cell components is more significant at the high potential transient conditions
- Bipolar plates have to have reasonable tolerance to these conditions.
- System design has to minimize these transient conditions. The question is: What is the cost to completely eliminate these transient conditions, if it is possible?

TreadStone's Coating with Precious Metals

--- Dotted Metal Plate Technologies



<u>Design Feature:</u>

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

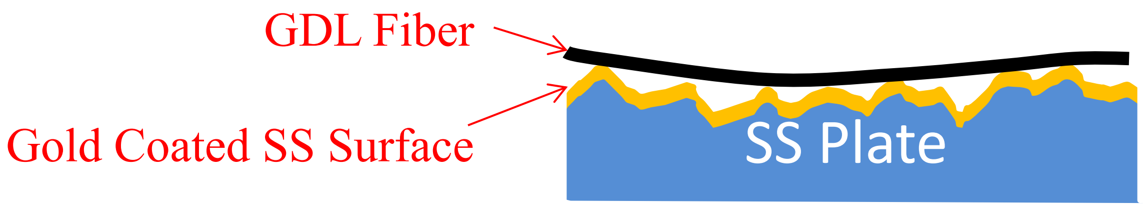
Graphite: 1375 $\mu\Omega$.cm

Gold: 2.2 $\mu\Omega$.cm

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

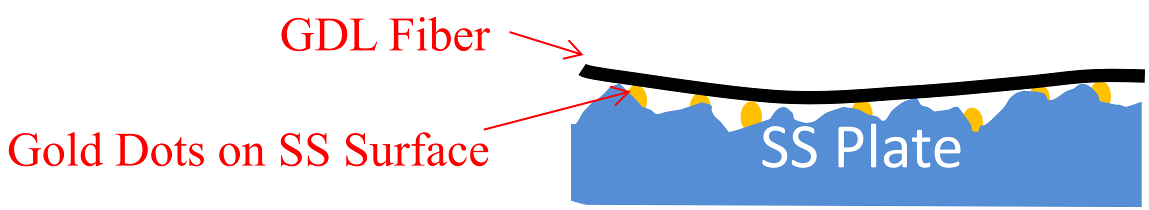
Actual Contact between GDL and Metal Plate

In micro scale, the GDL only in contact with metal plates at high points, of the rough surface of plates.



Majority of gold coated surface are not in contact with GDL.

On plates with gold dots on the surface: dots can standout out of the rough surface SS plate that have more chances to be contact with GDL.



Large amount of small gold dots can maintain sufficient contact points for low contact resistance.

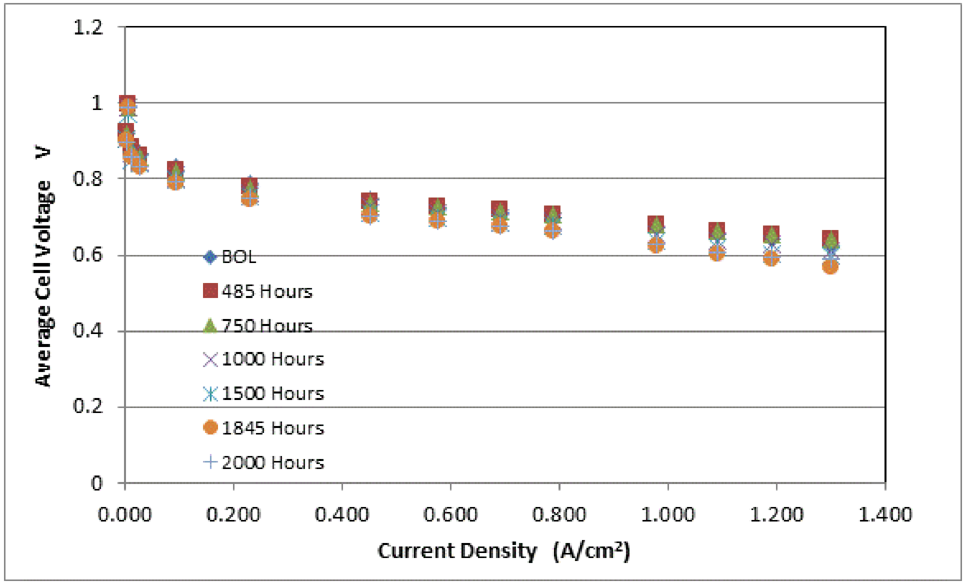
TreadStone Au-Dots Technology Ex-situ Test

Attribute	Metric	Unit	2015 DOE Target	Ford Data on Au-Dots
Corrosion anode	**Current density at active peak in CV**	μA/cm^2	<1	No active peak
Corrosion cathode	**Current density at 0.8 V_{NHE} in potentiostatic expt.**	μA/cm^2	<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.cm^2	<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

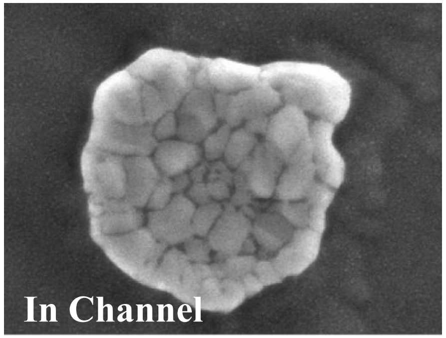
*RD: Rolling Direction

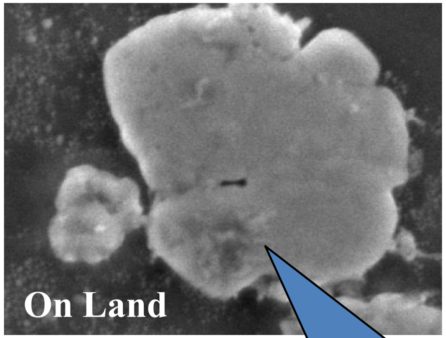
20-cell Stack Test at Ford

TreadStone Au-dot Plate Durability Test on 316L MP3 MBPP



Au splats on 1000 hrs. tested plate





Au splat pressed flatter in the stack, lead to the lower contact resistance.

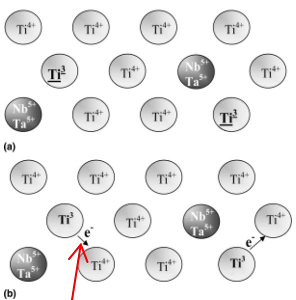
Contact Resistance [mΩ.cm^2]

Plate #		#18	#19	#17	#16	Average of all plates
Testing Time (hrs.)		500	1000	1500	2000	500-2000
TPV (mV)	BOL	9.09	8.49	7.42	8.12	8.41
	MOL	5.90	7.21	5.93	5.67	6.40

TreadStone's Coating without Precious Metals

--- Doped TiO_x Coating

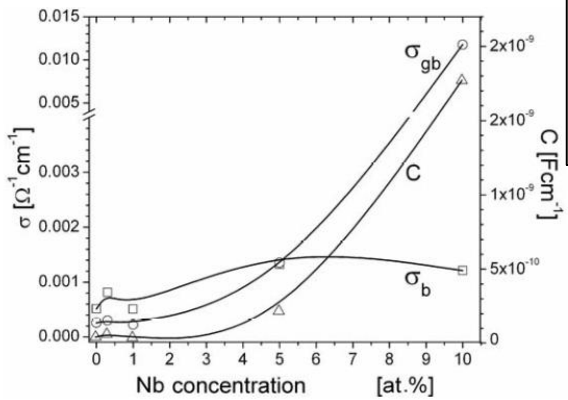
Doping TiO_2 with +5 valence elements will enforce the formation of Ti^{+3} in TiO_2 lattice structure, and result in higher electronic conductivities.



Electron hopping between Ti^{+3} & Ti^{+4} sites

Electrical conductance of Nb_2O_5 doped TiO_x

A. Trenczek-Zajac, M. Rekas, Materials Science-Poland, Vol. 24, No. 1, 2006



Challenges to use doped TiO_x coating:

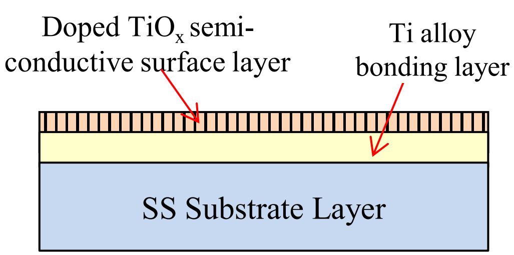
1. Doped TiO_x is semi-conductive. The electrical conductivity is not high enough.
2. How to obtain reliable bonding of doped TiO_x on metal substrate surface.

TreadStone's approach:

- To coat stainless steel substrate with Ti-Nb or Ti-Ta alloy. Then, grow the doped TiO_x surface layer on the Ti alloy coating layer.

1. The doped TiO_x on Ti alloy surface is thin and reliable.
2. Ti alloy bonding layer has excellent adhesion on metal substrate.

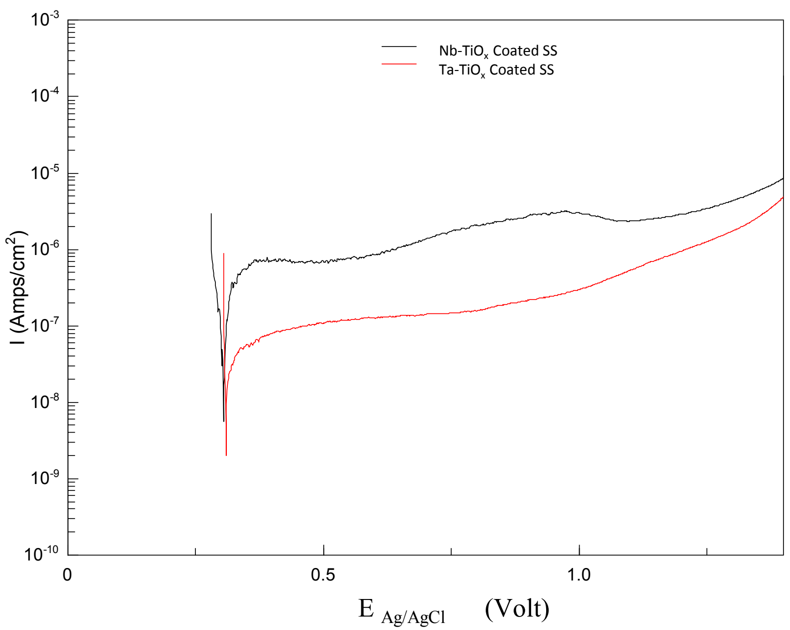
TreadStone's Coating Structure



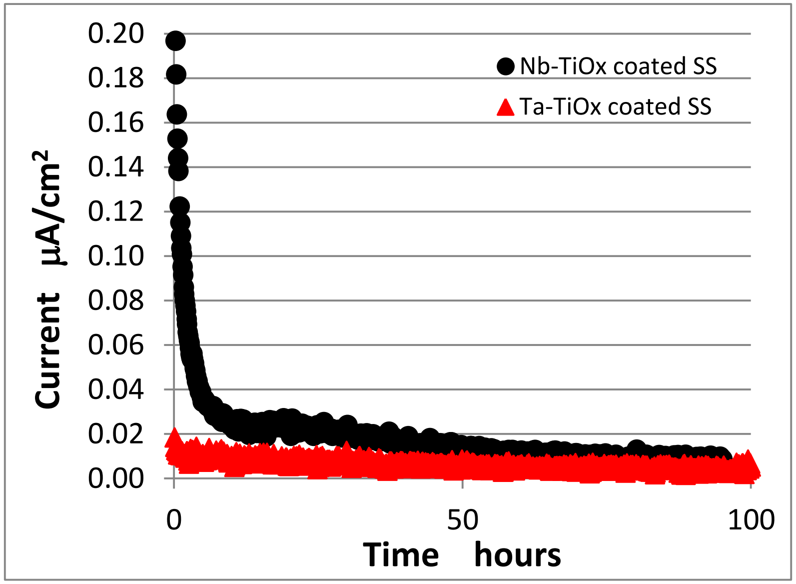
ex-situ Tests of Doped TiO_x coated SS

in pH 3 H_2SO_4 + 0.1 ppm HF at 80°C

Potentiodynamic Test (@10 mV/min)



Potentiostatic Test (@0.8V_{NHE})

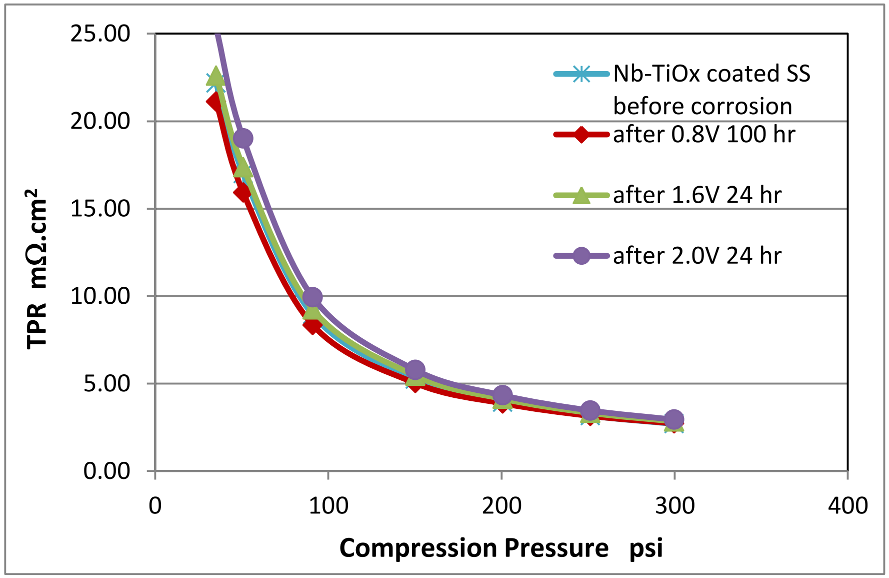


- Both Nb and Ta doped TiO_x coated SS can meet the corrosion current target (<1 µA/cm^2)
- Ta-TiO_x coated SS has lower corrosion current than that of Nb-TiO_x

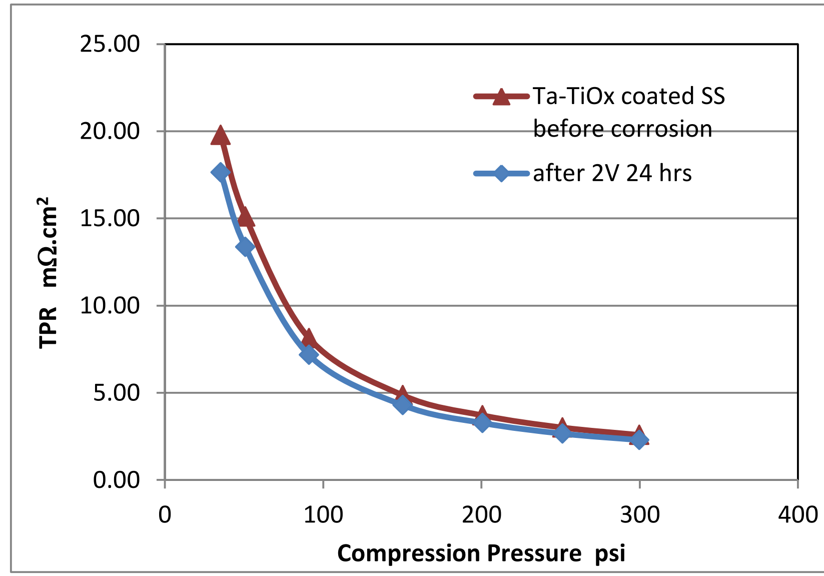
Doped TiO_x Coating Stability Test in Extreme Conditions

in pH 3 H_2SO_4 + 0.1 ppm HF at 80°C

316L SS with Nb-TiO_x coating before and after corrosion tests

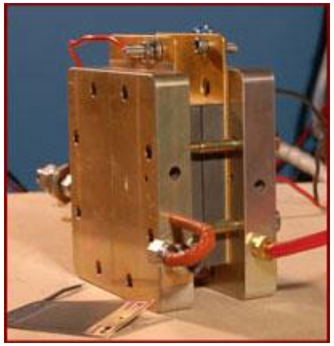


316L SS with Ta-TiO_x coating before and after corrosion tests

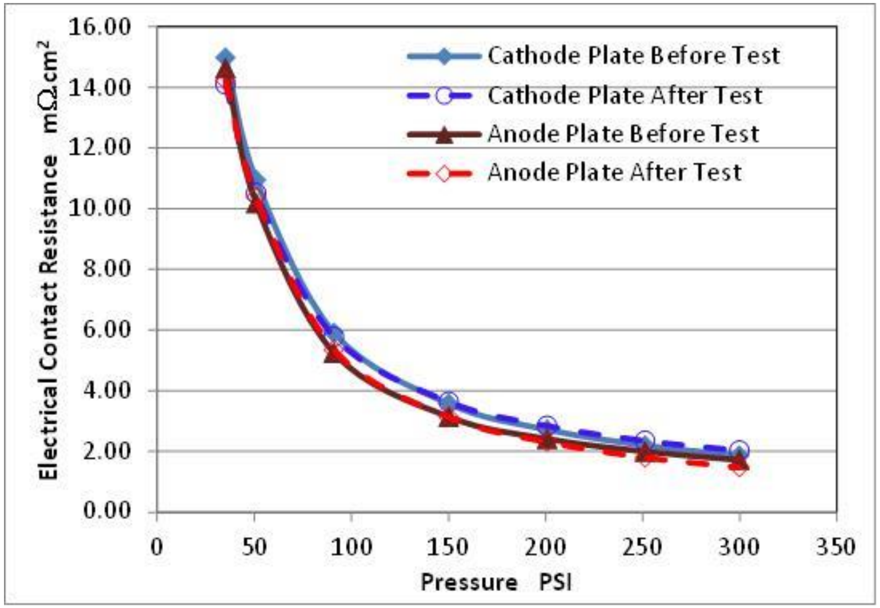


- Doped TiO_x coated SS has low surface electrical contact resistance.
- The coated SS has superior corrosion resistance for PEM fuel cell applications.
- The extreme corrosion condition (@ 1.6V_{NHE} or 2 V_{NHE}) *ex-situ* tests are not included in regular standard, but it is very attractive to OEMs because of the concerns of stack transient operation conditions.

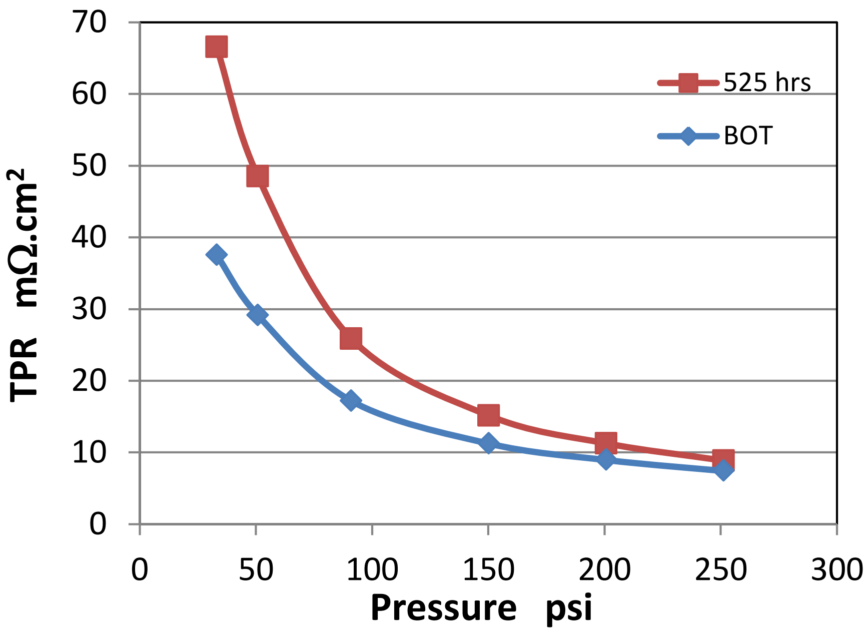
In-situ Cell/stack Test with Nb Doped TiO_x Coated SS Plates



Contact Resistance with GDL before and after 1,100 hrs. single cell test at consistent current



Through Plate Resistance with GDL before and after 525 hrs. 10-cell stack test at dynamic testing condition



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Summary

- TreadStone has developed low cost coating technologies for PEM fuel cell and electrolyzer applications.
  - ➢ DOTS technology has been thoroughly evaluated in PEM fuel cell and electrolyzer stacks. It is ready for commercialization.
  - ➢ TIOX technology has demonstrated superior corrosion resistance. Further development is focused on the manufacturing process and scientific mechanism investigation.
- Further technology development for commercialization:
  - ➢ Roll to roll coating process for low cost manufacturing.
    - The corrosion resistant coating must be capable to withhold the physical impact and substrate deformation during plate stamping.
    - Plate joining (welding) technology has to be compatible with the coating.
  - ➢ High production yield in continuous production.
  - ➢ Minimum capital investment for early market penetration.

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Acknowledgement

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