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Advanced Materials for PEM Electrolysis (H2-AMP)

tonbo

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### Performance Coatings for PEM Metallic Bipolar Plates Ton Hurkmans

Operator

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IHI GROUP

Short Company Introduction



Public company of Japanese origin; large industrial projects

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- PVD/PACVD service
- Shop-in-shop service



- PVD/PACVD equipment
- CVD equipment

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### Ionbond Worldwide Network



Ionbond Coating Centers

- All centers are ISO 9001 certified
- Additional certifications exist for specific markets, including ISO/TS 16949 (automotive) ISO 13485 (medical) EN 9100 / AS 9100 (aerospace) NADCAP (aerospace) ISO 14001

### Coating service portfolio

Automotive

impact.

DLC coatings for increased engine efficiency and

reduced environmental



Forming and Molding

**Deco, Sport & Luxury** Decobond<sup>™</sup> Series

Superior hardness, wear resistance, and a metallic look.

#### **Cutting Tools**

For every machining requirement and work piece material, from low to extremely high cutting speeds.

#### Fuel Cell & Electrolyzer

Protective coatings with high performance and durability for metallic bipolar plates

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# Bipolar Plates (BPP)

- Main challenges for PEM technology
  - Cost reduction
  - Weight reduction
  - Durability improvement
- Attention to Bipolar Plates
  - Substantial fraction of the total cost
  - Heaviest component
  - Providing physical strength

#### Mercedes-Benz GLC F-CELL



Source: www.greencarcongress.com

## Typical Bipolar Plate Materials in PEM Stacks

- Graphite (Fuel Cells)
  - Limitations in mechanical strength (brittle in nature)
  - Not great for mobile applications of fuel cells
  - High machining costs
- Titanium
  - Expensive
  - Moderate formability
  - H<sub>2</sub> embrittlement
- Stainless Steel
  - Suitable mechanical properties
  - Good formability
  - High level of intrinsic corrosion resistance
  - Good electrical conductivity

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• Affordable

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# Need for coating of metal BPP

#### • Enhanced corrosion resistance

- Inhibits harmful ions out-diffusion from stainless steel BPP
- Inhibits hydrogen absorption and embrittlement of Ti BPP
- Low and steady electrical contact resistance over the lifetime of the stack
  - Low internal ohmic loss at high current density
  - Efficient and stable hydrogen to electricity conversion (FC)
  - Efficient and stable hydrogen generation (EL)

Chapter 2

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# The Challenge for Coatings . . .

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### Challenging Operation Conditions for BPP's

- Mass volume PEM Fuel Cell (passenger cars); expected lifetime
- Demanding application (trains, trucks, aerospace); expected lifetime
- Electrolyzers;

expected lifetime

5.000 – 10.000 hr 20.000 – 30.000 hr > 80.000 hr

### Challenging Operation Conditions for BPP's

- Acids (pH 2 to 4)
- Humidity
- Cell operating voltages, <u>especially for electrolyzers</u>
- Elevated temperatures
- Corrosion Rate < 1  $\mu$ A.cm<sup>-2</sup>
- High Current densities > 2 A. cm<sup>-2</sup>
- Low ICR < 10 m $\Omega$ . cm<sup>2</sup>
- Low Hydrogen Permeability < 2E<sup>-6</sup> cm<sup>3</sup>/cm<sup>2</sup>.s

### One Coating Solution should cover all requirements! ionbond

# Coating Designs

- Use conductive materials in order to obtain the high current densities and low ICR
- Build a diffusion barrier layer to avoid metal ions leaching and/or H2 embrittlement
- Make a perfectly closed layer system in order to avoid pitting corrosion and possibly coating adhesion losses
- If there would be defects, give the coating "self-healing" properties to self repair damages
- There is a basic conflict in the design criteria of a coating:
  - Corrosion resistance calls for low electrochemical conductivity
  - Electrical power requirements call for a high electrical conductivity

### Coatings in the Market Place (and more)

- Electroplating
  - Au
  - Pt

- PVD/CVD/PACVD
  - Au
  - TiN
  - CrN
  - Carbon
  - Max Phase

- Other
  - Nitriding / Carburizing
  - Pack cementation
  - Thermal Spray

### Chapter 3 Coatings from lonbond; Current Focus

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# Ionbond coatings for Bipolar Plates, PTL's, and Current Collectors

- Ti + Carbon by PVD
  - Typically for stainless steel
  - Medium Lifetime expectation (Passenger Cars)
- DOT<sup>™</sup> Technology (Thermal Spray)
  - For stainless steel (Ti-PVD + DOTs)
  - For Titanium (DOTs only)
  - Extreme Lifetime expectation (Trucks, Buses, Trains, *Electrolyzers*)



### Carbon based Coatings by PVD

#### Batch load of Bipolar Plates



#### Coating Architecture of Carbon Coatings



~50 nm Carbon ~100 nm Metal Base layer

#### Stainless Steel BPP

- 3 step process
  - Thermal spray of splashes/droplets of Au on cathode side



#### • 3 step process

- Thermal spray of splashes/droplets of Au on cathode side
- Thermal spray of splashes/droplets of Pt on anode side



#### 3 step process •

- Thermal spray of splashes/droplets of Au on cathode side
- Thermal spray of splashes/droplets of Pt on anode side



#### • Post-oxidation of Ti to form a diffusion/corrosion barrier of TiO<sub>2</sub>

- Final Result Split in functionality through the coating architecture
  - High corrosion resistance through TiO<sub>2</sub>
  - Virtually no H<sub>2</sub> uptake on cathode side as it is blocked by TiO<sub>2</sub>
  - Low electrical resistance through the Au and Pt contact points, i.e. electrically conductive pathways



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### Droplet spray unit



### DOT Coating – SEM Images

- Gold droplets are deposited with thermal Spray onto the surface and form splats with diameter from  $1-5\ \mu\text{m}$
- The cross section shows that the thickness is in the range 0.1 0.3  $\mu m$

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### Corrosion test overview

- Medium H<sub>2</sub>SO<sub>4</sub>; pH 3
- 20 ppm Cl<sup>-</sup>
- 10 ppm F<sup>-</sup>
- Reference electrode Ag/AgCl (0.2 V shift)
- Dynamic polarization
  - from -0.4 to +0.6 V
  - OCP; open circuit potential
  - Icorr; corrosion current at OCP
- Static polarization
  - 24 hr at 0.6 V
  - DOE;  $I_{static}$  below 1  $\mu$ A

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### Polarization curves Au DOT's coating

- DOT Samples were produced with Ti base layer on Stainless Steel 316.
- Thicknesses applied were 50 nm, 100 nm and 200 nm Ti.
- Dynamic polarization curves were very similar for all three Ti thicknesses:
  - OCP around 400 mV
  - Icorr around 0.05  $\mu\text{A/cm}^2$

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• Dynamic polarization curves at least as good after static polarization

#### Z E

#### Ex-Situ Beschichtungsbenchmark Kontaktwiderstand und Korrosionsstrom Probe A



### ICR unit developed at lonbond

- The unit is suitable to measure complete Bipolar Plates, also very large ones
- It can measure ICR at 2 sides
- it can measure ICR at only one side





### ICR dependence on Au surface coverage

 Interface contact resistance ICR is at acceptable level already at Au surface coverage of 2%



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### Chapter 4 What to expect next? DOE Focus/opportunities

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### Opportunities going forward

- Ongoing pressure on
  - Higher electrical current densities
  - Longer lifetime of stacks
  - Cost reductions

### Opportunities going forward – Vacuum Deposition

- PVD, CVD, and PACVD based coatings:
  - Precious metals free solutions
  - Solve the natural conflict between high electrical currents and no electrochemical corrosion
  - Withstand the high electrical operating voltages in electrolyzers
    - Coatings should not be dissolved ("stripped")
    - Shift in polarization curves, accelerating pitting corrosion, which can also lead to coating adhesion failures

- Further voids reductions of deposited coatings
  - reduced dust while processing (creating spots with missing coating)
  - no droplets (= larger metal clusters embedded in the coating system)
  - pinholes elimination, because they are an easy path for pitting corrosion
- Self-healing systems ("voids repair themselves through oxidation and seal again")

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# Opportunities going forward – DOT's Thermal Spray

- DOT's thermal spray
  - Ongoing precious metal transfer efficiency improvements (equals cost reductions):
    - Sticking factor of incoming particles
    - Minimizing over-spray outside the active area of the bipolar plate
  - Optimization of droplet shapes to have maximum performance







• Upscaling to higher throughputs

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### Thank you for your interest!

Operator

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For follow up: Ton.Hurkmans@ionbond.com

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