TECHNOPORT 2012
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2012

rerc 2012

On the corrosion and contact resistance characteristics of micro-stamped metallic bipolar plates

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Related Publications

- MF Peker, ON Cora, **M Koç**, (2011), ‘Investigations on the Variation of Corrosion and Contact Resistance Characteristics of Metallic Bipolar Plates Manufactured under Long-run Conditions’, *International Journal of Hydrogen Energy, doi:10.1016/j.ijhydene. 2011.08.067*

- C Turan, ON Cora, **M Koç**, (2011), ‘Effect of Manufacturing Processes on Contact Resistance Characteristics of Metallic Bipolar Plates in PEM Fuel Cells’, *International Journal of Hydrogen Energy, v36, n19, September 2011, pp. 12370-12380*

- E Dur, ON Cora, **M Koç**, (2011), ‘Experimental Investigations on the Corrosion Resistance Characteristics of Coated Metallic Bipolar Plates for PEMFC’, *International Journal of Hydrogen Energy, v26, pp. 7162-7173*

- E Dur, ON Cora, **M Koç**, (2011), “Effect of manufacturing conditions on the corrosion resistance behavior of metallic bipolar plates in proton exchange membrane fuel cells”, *Journal of Power Sources, v.196 (2011), pp.1235–1241*

- ON Cora, S Mahabunpachai, **M Koç**, (2010), “Effect of Manufacturing Processes on Formability and Surface Topography of Proton Exchange Membrane Fuel Cell Metallic Bipolar Plates”, *J. Power Sources, v.195, pp. 5269-5277.*

Related Publications

- F Dundar, S Mahabunphachai, E Dur, **M. Koc**, (2009), “Corrosion Resistance Characteristics of Stamped and Hydroformed PEMFC Metallic Bipolar Plates”, *Journal of Power Sources, v.195, pp.3546-3552.*

- **M. Koç**, S. Mahabunphachai, and F. Dundar, (2009), “PEMFC Metallic Bipolar Plates: Effect of Manufacturing Method on Corrosion Resistance”, *ECS Transactions, v. 25, n.1, pp.1773-1782.*

- S. Mahabunpachai and **M. Koç**, (2008), “Fabrication of Micro-channel Arrays on Thin Metallic Sheet Using Internal Fluid Pressure: Investigations on Size Effects and Development of Design Guidelines”, *J of Power Sources, v.175, n.1, pp.363–371 (Jan 2008)*

- **M. Koç** and S. Mahabunpachai, (2007), **“**Feasibility investigations on a novel micro-manufacturing process for fabrication of fuel cell bipolar plates: internal pressure-assisted embossing of micro-channels with in-die mechanical bonding**”,** *Journal of Power Sources, v.172, n.2, pp. 725–733 (Oct 2007)*

Outline

- **INTRODUCTION**:
  - Background Information: Fuel Cells, PEMFCs
  - Bipolar Plate (BPP) manufacturing

- **CORROSION RESISTANCE OF BPP's**
  - Uncoated Case
  - Coated Case
  - Effect of Process Sequence
  - Conclusions

- **CONTACT RESISTANCE OF BPP's**
  - Uncoated Case
  - Coated Case
  - Effect of Process Sequence
  - Conclusions

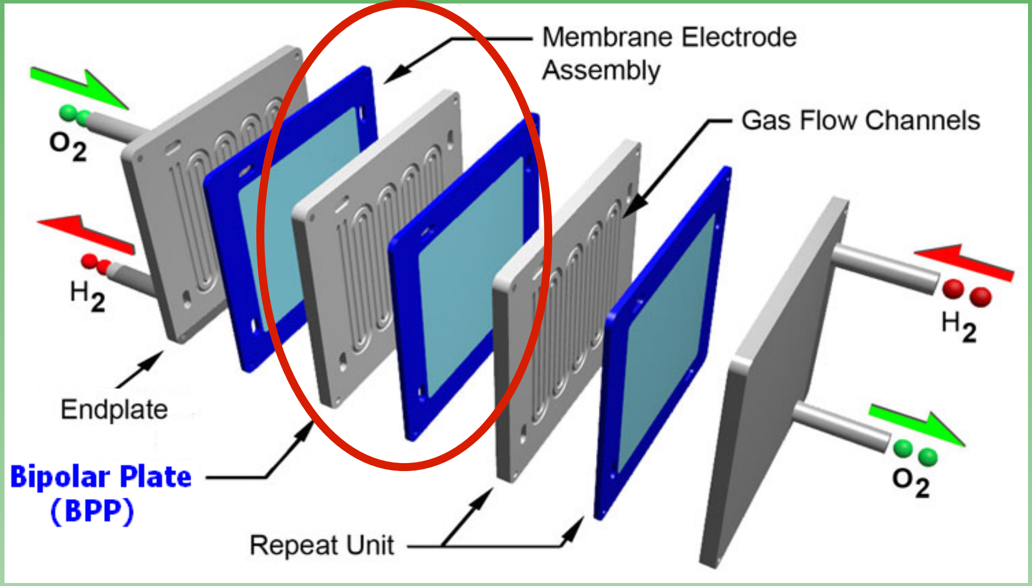
- **Acknowledgments**

Challenges in FC Technology

- **4-10 times more expensive than internal combustion engines**

  ($200 to $300 per kW, as compared to $30-to-$50 per kW)

- Ream; 2007
- Scherer et al.; 2007



- **BPPs constitutes 60-80% of the stack weight, 50% of the stack volume and 25-45% of the stack cost.**

- Tsuchiya & Kobayashi, 2004
- Li & Sabir, 2005
- Antunes et al., 2010

- **Need for robust, cost-effective, mass production technology for manufacturing of bi-polar plates.**

Issues and Requirements for BPPs

Issues

- Cost
- Contact resistance
- Corrosion resistance
- Wetting properties
- Flow field design
- Mechanical properties
- Reactant permeation
- Bulk electrical conductivity
- Manufacturing

Brett and Brandon, Journal of Fuel Cell Science and Technology. 4 (2007) 29-44.

DOE Goals

Characteristic	Units	2010 Goal	2015 Goal
Cost	\$ / kW	5	3
Weight	kg / kW	<0.4	<0.4
H_2 permeation flux	$cm^3\ sec^{-1}\ cm^{-2}$ @ 80°C, 3 atm (equivalent to <0.1 mA / cm2)	$<2 \times 10^{-6}$	$<2 \times 10^{-6}$
Corrosion	$\mu A / cm^2$	<1	<1
Resistivity	Ohm-cm	0.01	0.01
Flexural Strength	MPa	>25	>25
Flexibility	% deflection at mid-span	3 to 5	3 to 5

www.eere.energy.gov

Materials for Bipolar Plates

Material	Advantages	Disadvantages
Graphite	Low contact resistance High corrosion resistance	Expensive to machine Brittle Thick
Carbon-carbon composites	Excellent corrosion resistance Low bulk resistivity Low contact resistance	Poor mechanical properties (brittleness) Porosity High weight and volume High processing cost
Carbon-polymer composites	Low cost Good corrosion resistance Low weight No machining process Commercial availability of the raw materials	Low mechanical strength Low electrical conductivity
Metals	**Good electrical conductivity** **High thermal conductivity** **Low cost** **Excellent mechanical properties** **Ease of fabrication** **Lightweigth and less bulky**	**Severe corrosion** **Contact resistance**

Yuan et al., J. New. Mat. Electrochem. Systems. 8 (2005) 257-267.

Research Motivation and Objectives

Motivation

- PEMFC is a promising energy generation technology
- BPP is a critical component in PEMFCs
- Corrosion and Contact Resistance are major problems with metallic BPP for PEMFCs
- There are studies on corrosion and contact resistance of metallic BPPs
- ***However, none addresses the effect of manufacturing process***

Objectives are understanding the followings on Corrosion and Contact Resistance of metallic BPPs

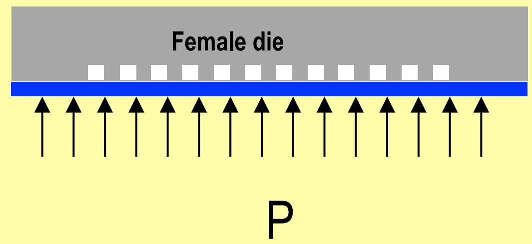
- Effect of material, manufacturing process and process parameters
- Effect of coating and its interactions with manufacturing conditions
- Effect of process sequence

Research Plan

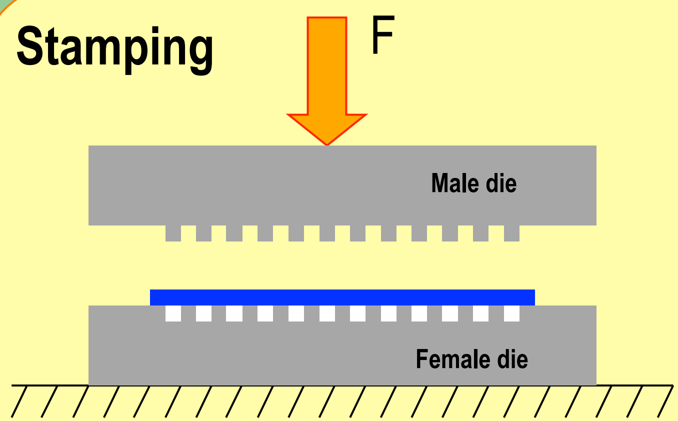
Uncoated BPP Materials:
- SS304
- SS316(L)
- SS430
- Ni270
- Ti gr.1&2

BPP with coatings:
- CrN
- TiN
- ZrN

Hydroforming



Stamping



Formability & dimensional variations analyses

Contact resistance analyses

Corrosion resistance analyses

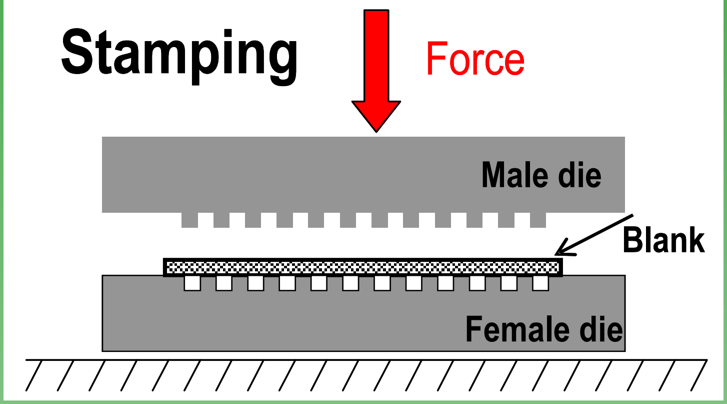
Durability and performance analyses

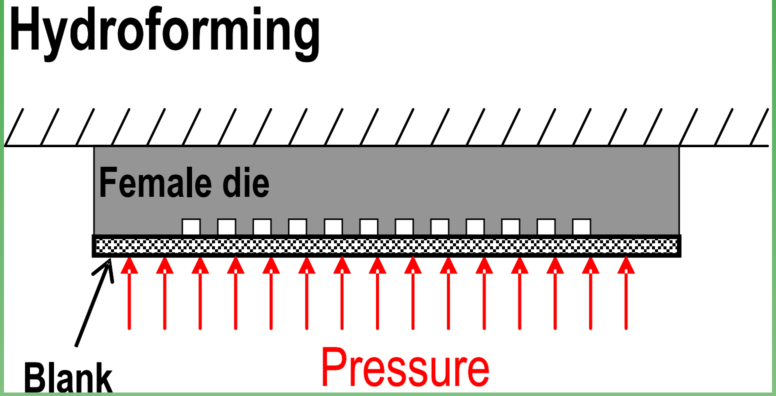
Existing Studies on Corrosion Resistance

Material	Sample Form	Reference
SS304	**Unformed coupon**	*Joseph et al., 2005*
SS304	**Unformed sheet**	*Garcia et al., 2006*
SS316L and amorphous $Zr_{75}Ti_{25}$	**Unformed sheet and bulk**	*Lafront et al., 2007*
SS316L, SS310S, SS904L, SS304,	**Unformed**	*Pazio and Silva, 2007*
SS304	**Unformed plate**	*Ren and Zeng, 2007*
SS316L	**Unformed plate**	*Wang and Northwood, 2006*

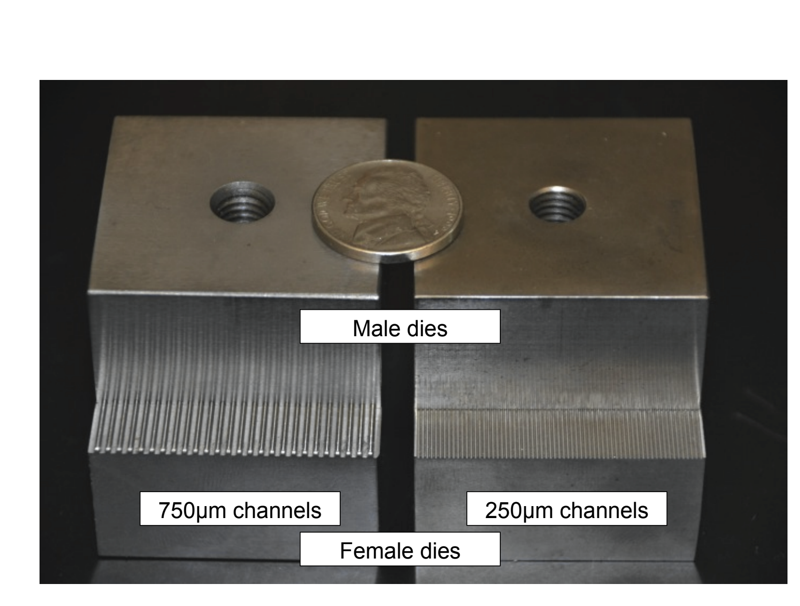
studies on the effects of manufacturing ???

Experiments- Manufacturing conditions





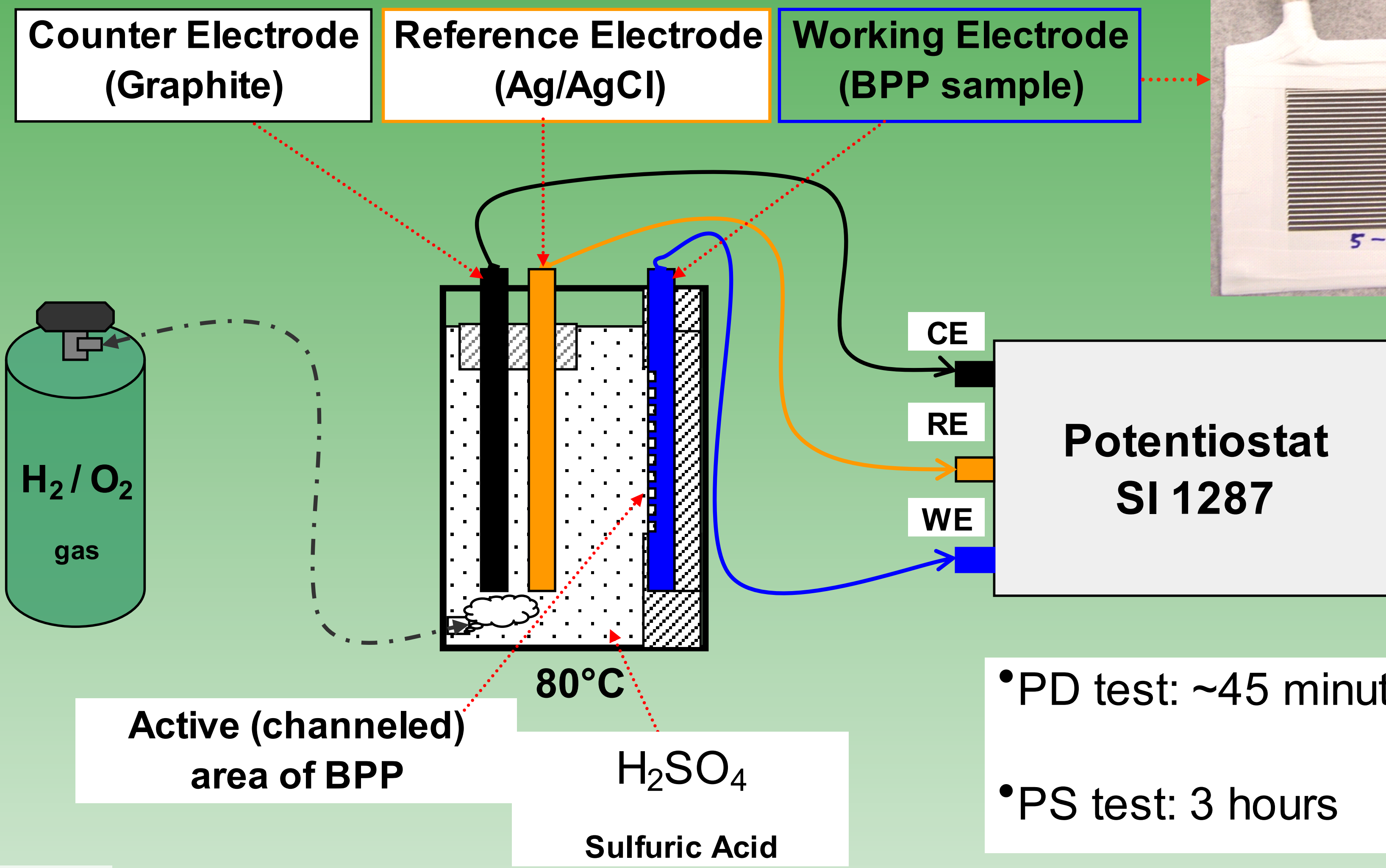
100, 200, 300 kN
0.1 and 1 mm/s

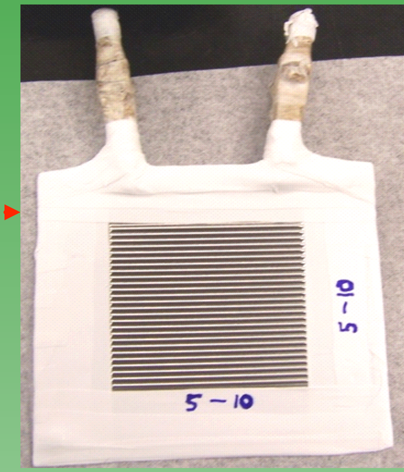


20, 40, 60 MPa
0.1 and 1MPa/s

- BPP Materials: SS 304, SS430, SS316L, Ti, Ni (51µm-thick-uncoated)
- Coating Materials and Thicknesses: TiN, CrN, ZrN / 0.1, 0.5, 1 µm (51µm-thick-coated-SS316L)

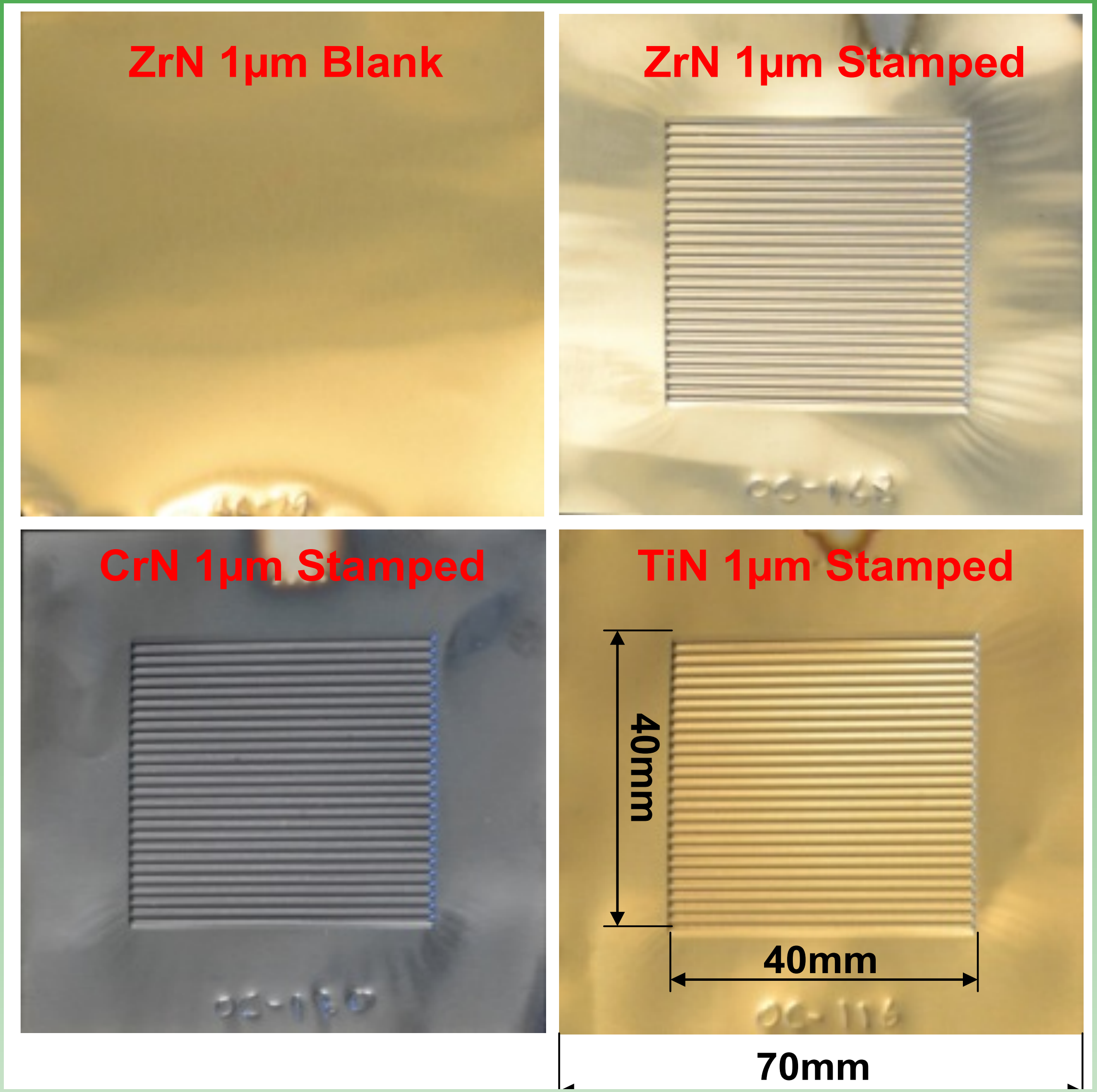
Experiments- Corrosion Test Setup





- PD test: ~45 minutes
- PS test: 3 hours

Coated Bipolar Plates



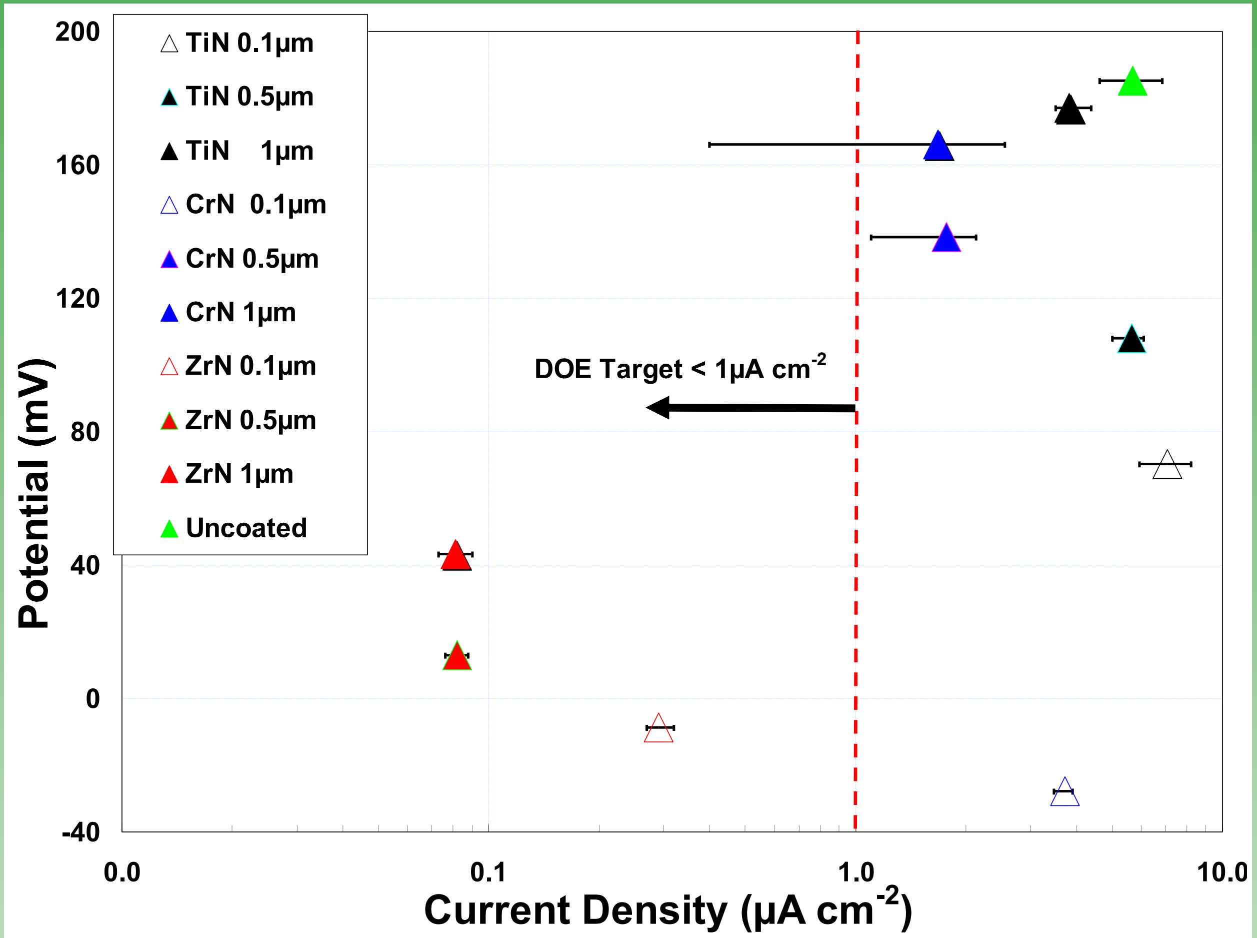
<u>COATING</u>

Coating Method: PVD (Physical Vapor Deposition)

Coating Materials: TiN, CrN, ZrN

Coating Thickness: 0.1, 0.5, 1 µm

Effect of Coating Type & Thickness (Coated BLANK)



- F. Dundar, E Dur, S. Mahabunphachai, M. Koç, (2010), J Power Sources, v195, pp.3546-3552.
- E Dur, O N. Cora, M. Koc¸ (2011), J Power Sources, v196, pp.1235–1241.

ZrN > CrN > TiN

1 micron > 0.5 micron > 0.1 micron

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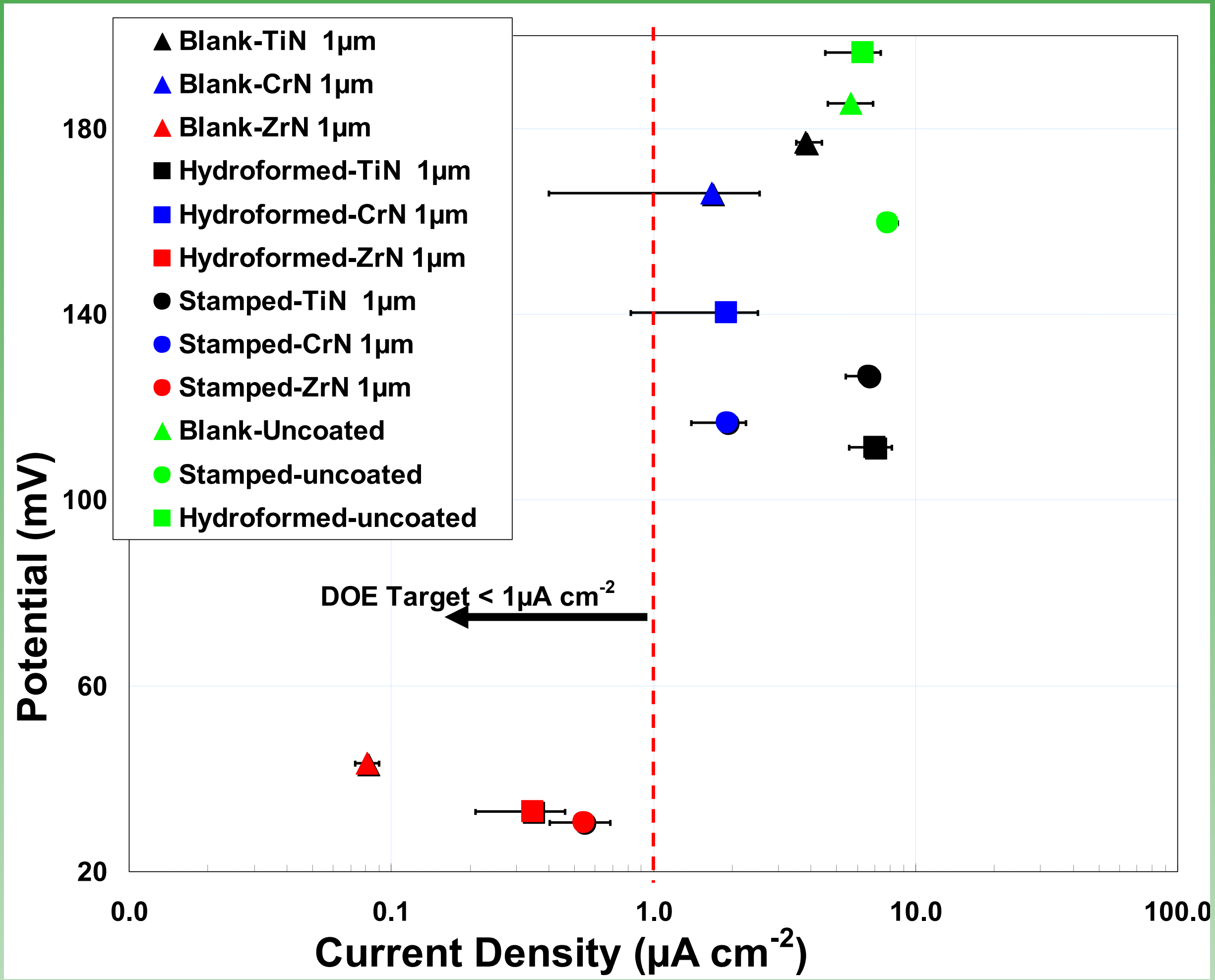
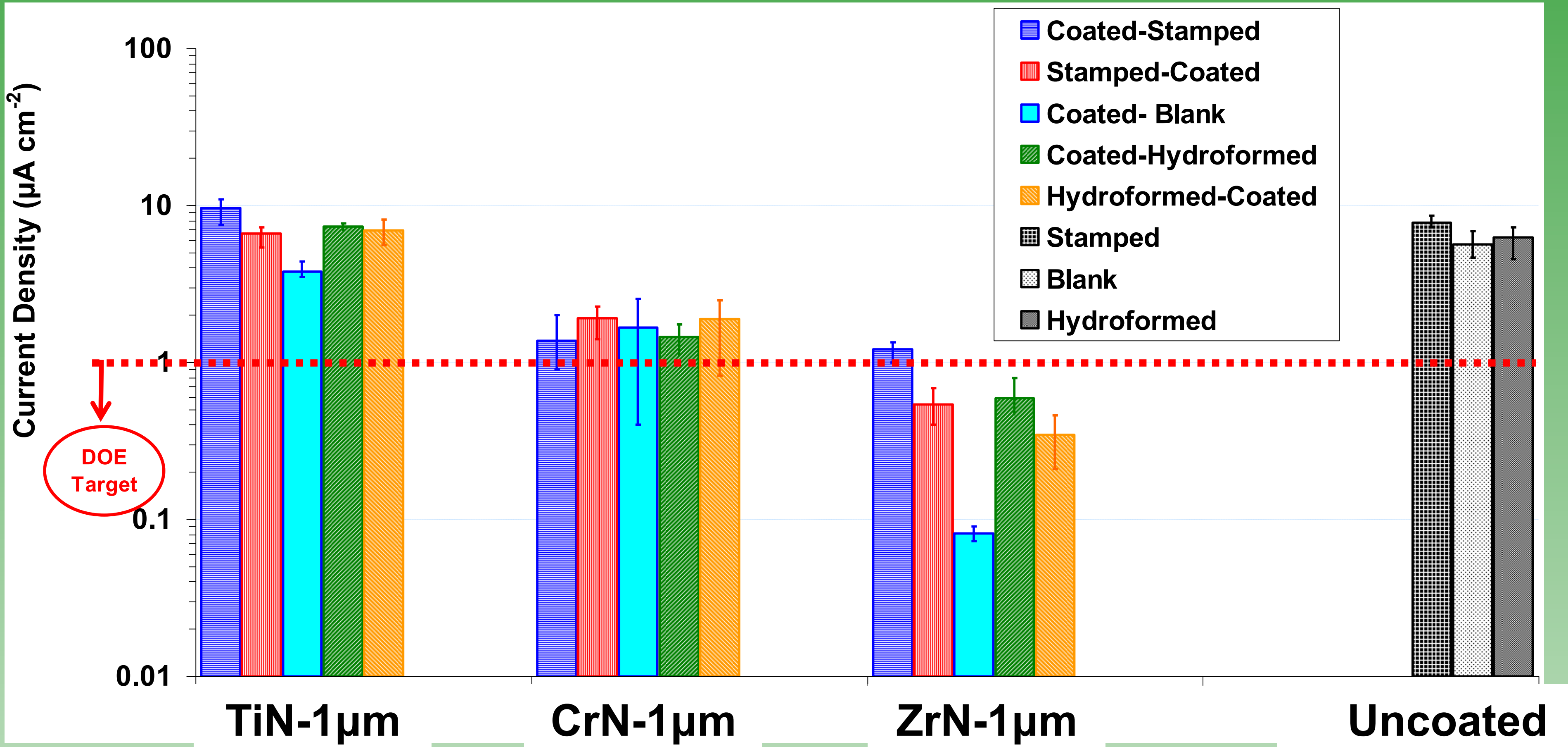
Effect of Manufacturing (Coated BPPs)



- F. Dundar, E Dur, S. Mahabunphachai, M. Koç, (2010), J Power Sources, v195, pp. 3546-3552.
- E Dur, O N. Cora, M. Koc¸ (2011), J Power Sources, v196, pp.1235–1241.

Blank > Hydroformed > Stamped (ZrN)

Process Sequence (Formed-Coated vs. Coated-Formed)



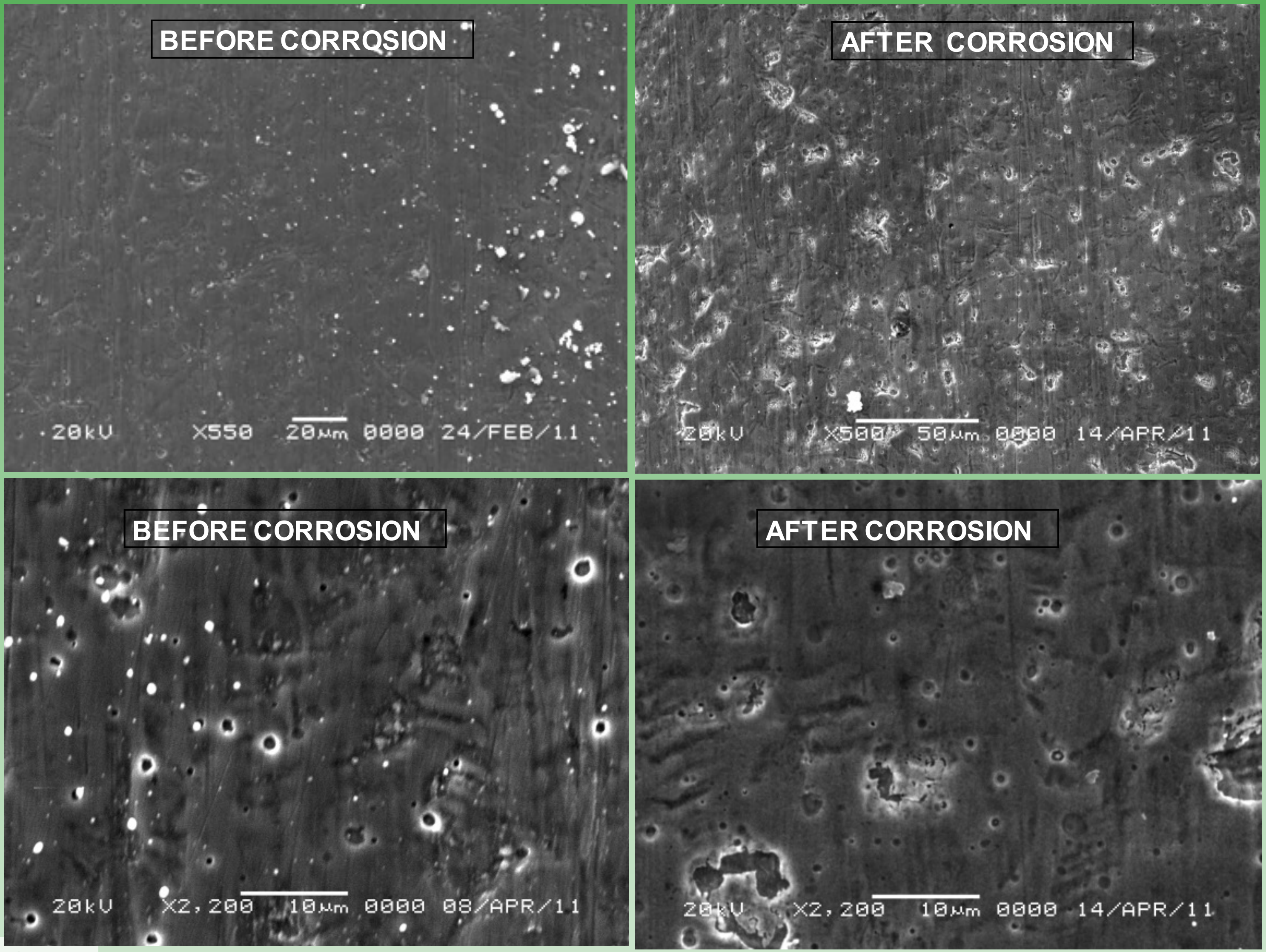
Formed-Coated > Coated-Formed insignificant for Hydroformed

Hydroformed > Stamped for ZrN (significant)

ZrN > CrN > TiN (significant)

SEM Images for Coated BPPs

TiN 1μm-Hydroformed-Coated



Conclusions

Effects of manufacturing processes and substrate materials (Uncoated BPPs):

- Blank samples showed the best corrosion resistance
- Manufacturing process and parameters had an adverse impact

- SS316L, Ti, SS304 > Ni, SS430 (significant)
- Hydroformed > Stamped (slightly)

- **Uncoated samples do not meet the DOE target**

Conclusions

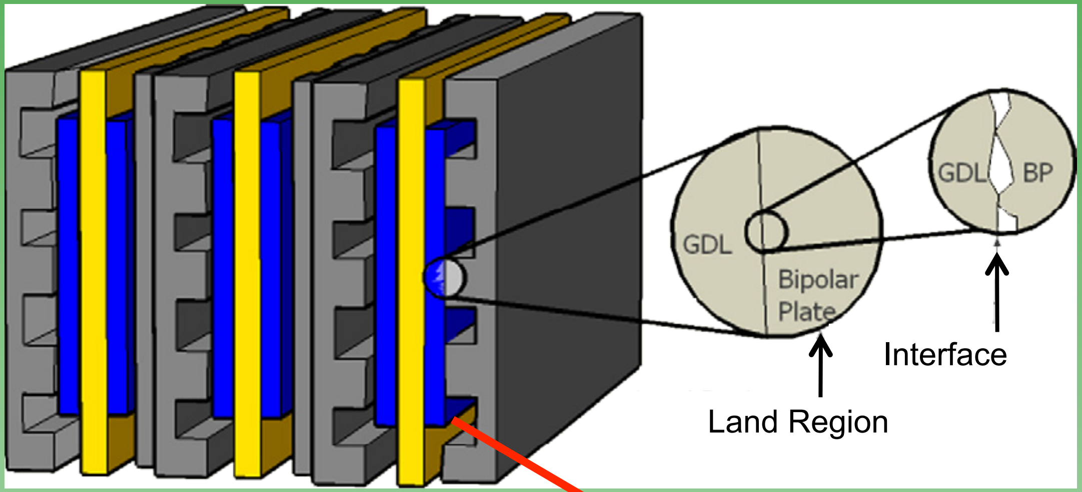
Effects of coatings, manufacturing processes and process sequence (Coated BPPs):

- ZrN > CrN > Uncoated > TiN (significant)
- 1 micron > 0.5 micron > 0.1 micron thickness (significant)
- Blank > Hydroformed > Stamped
- Formed-Coated > Coated-Formed (*insignificant for hydroforming*)
- BPPs with 250 micron > BPPs with 750 micron (insignificant)

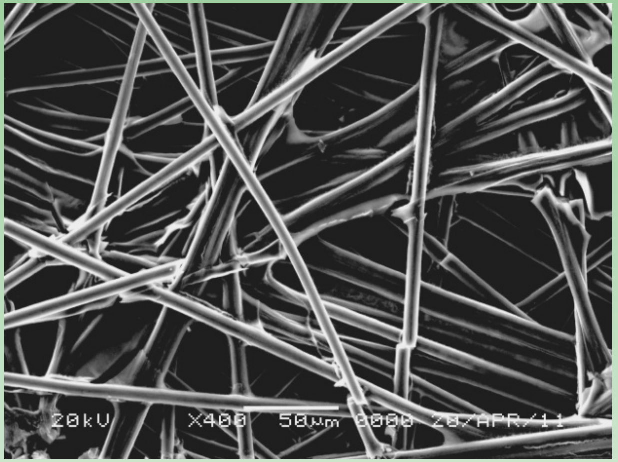
ZrN and CrN coatings meet the DOE target

Contact Resistance (ICR) in BPP

PEMFC Stack



Gas diffusion layer (GDL)

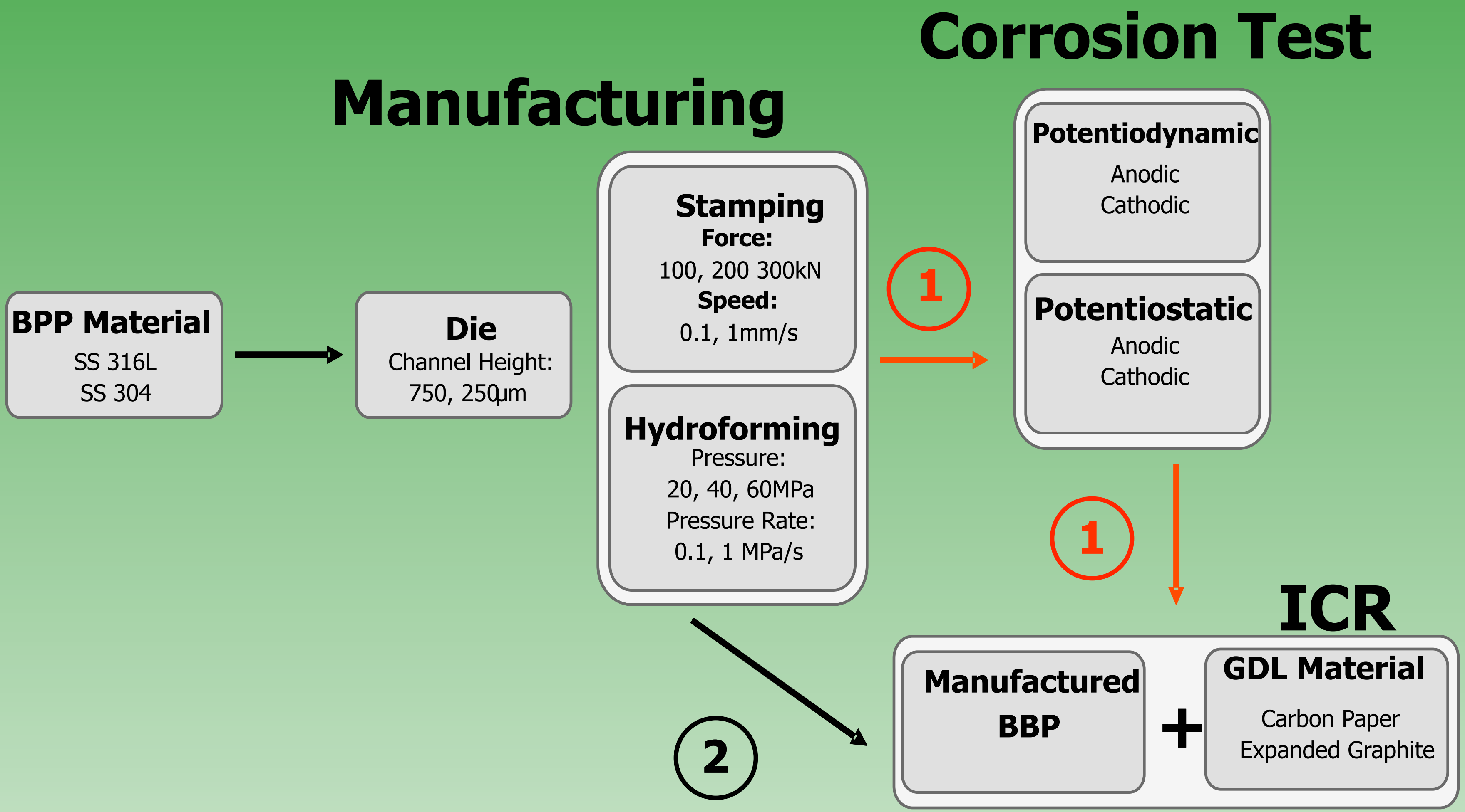


Effects of contact resistance

- Increase voltage drops
- Decrease efficiency
- Decrease power outputs
- Decrease power density

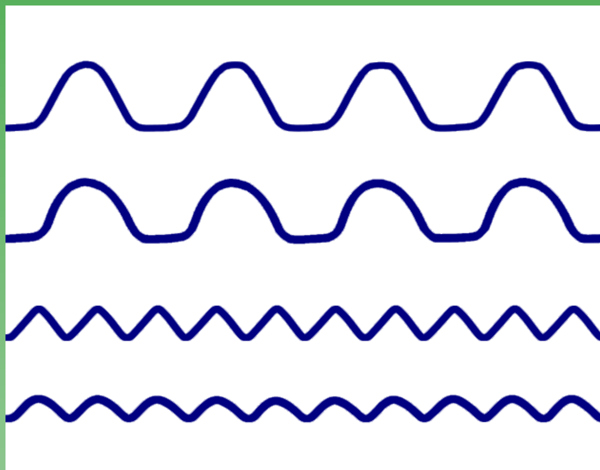
Avasarala et al., J. Power Sources. 188 (2009) 225-229.

Methodology-Uncoated BPP



***C. Turan**, Ö. N. Cora, M. Koç, has been accepted with revision by International Journal of Hydrogen Energy in 2011.*

BPP Channel Profiles

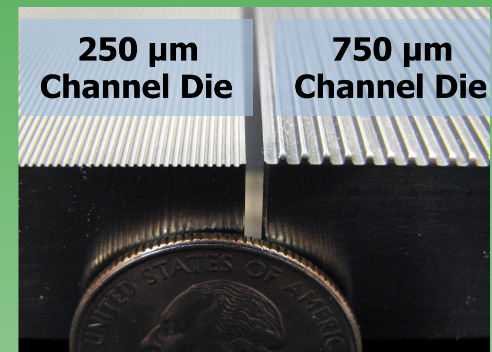


Stamped 750 µm Channel

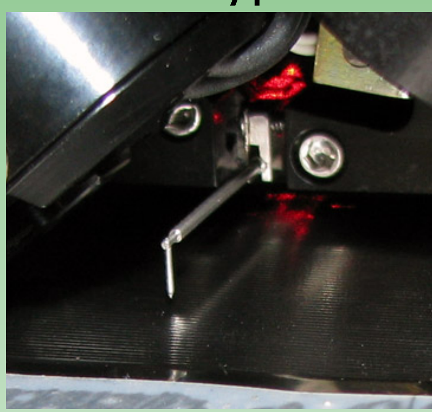
Hydroformed 750 µm Channel

Stamped 250 µm Channel

Hydroformed 250 µm Channel

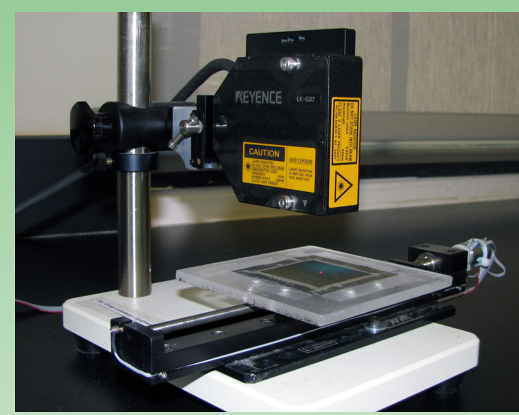


Contact Type Profiler



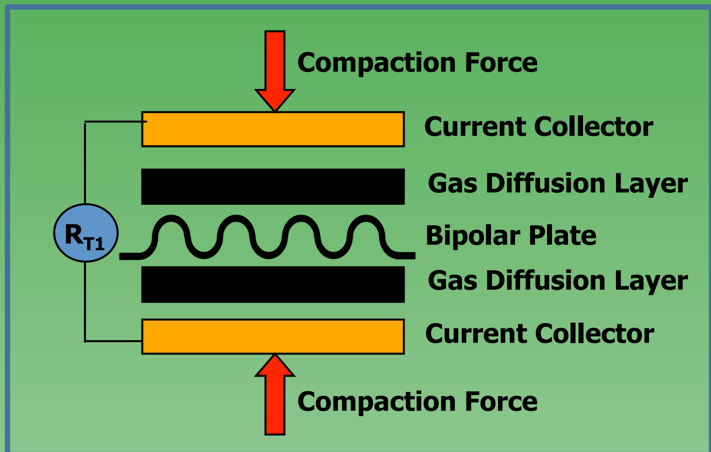
Stylus Profiler (Ambios XP1)
Vertical Resolution 6.2nm at 400 μ m

Non-Contact Measurement



Laser Displacement Sensor (Keyence G37) with
Motorized stage (National Aperture MM-4M-EX-140)
Repeatability 0.01 μ m

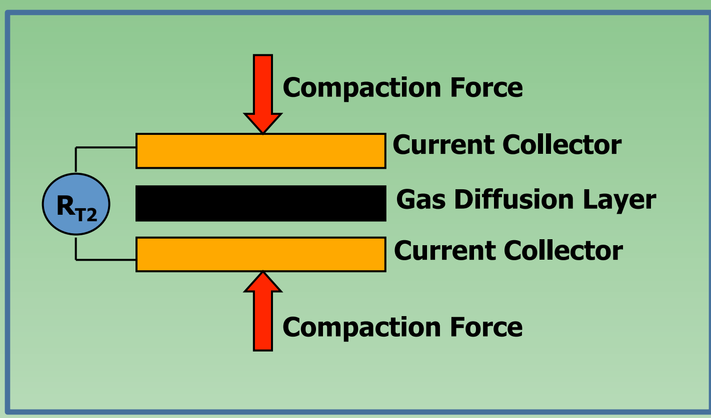
Contact Resistance Tests

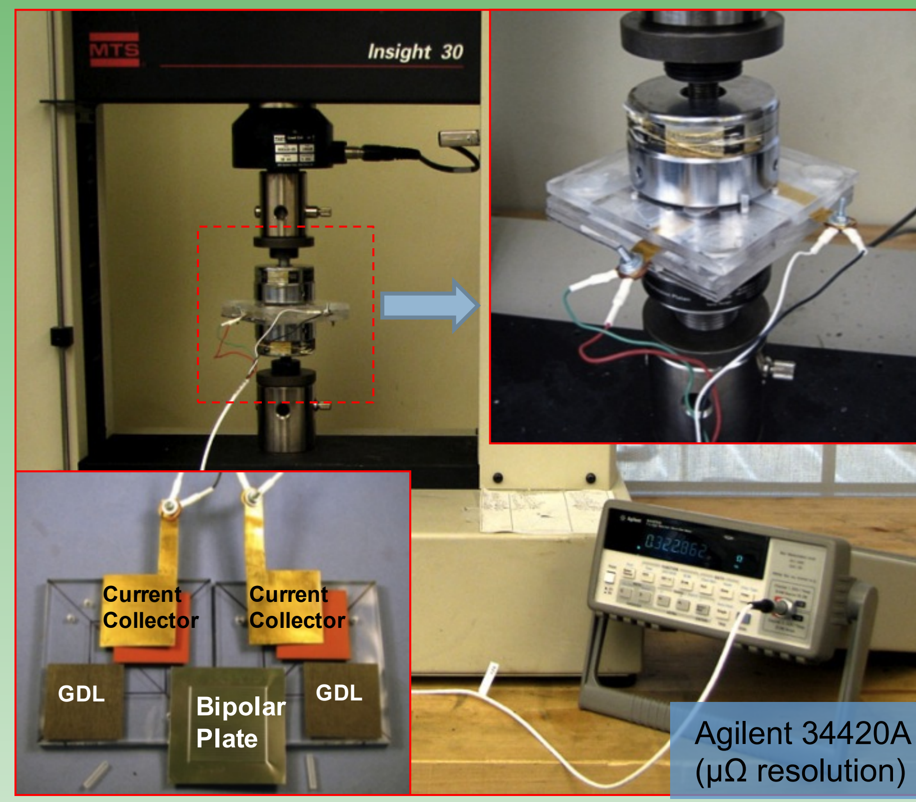


$$R_{T1}=2R_{CC}+2R_{CC/GDL}+2R_{GDL}+2R_{GDL/BPP}+R_{BPP}$$

$$R_{T2}=2R_{CC}+2R_{CC/GDL}+R_{GDL}$$

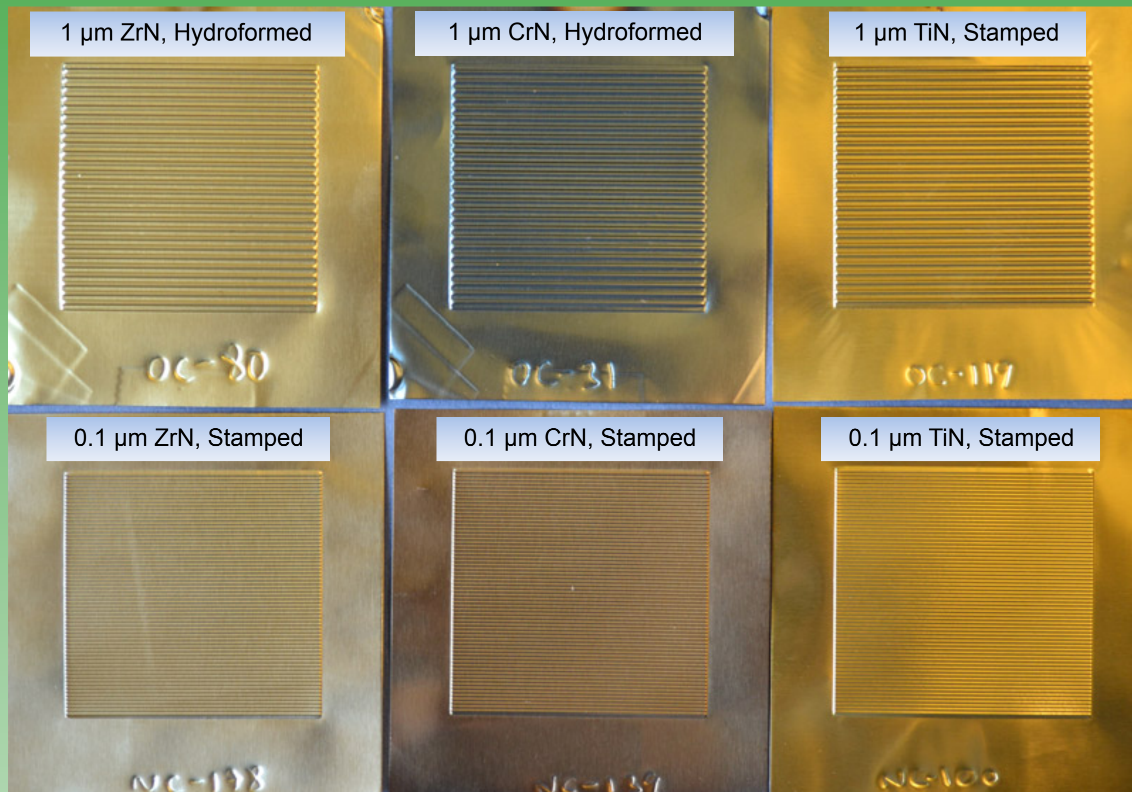
$$R_{BPP/GDL}= 0.5\ (R_{T1} - R_{T2} - R_{GDL} - R_{BPP})$$





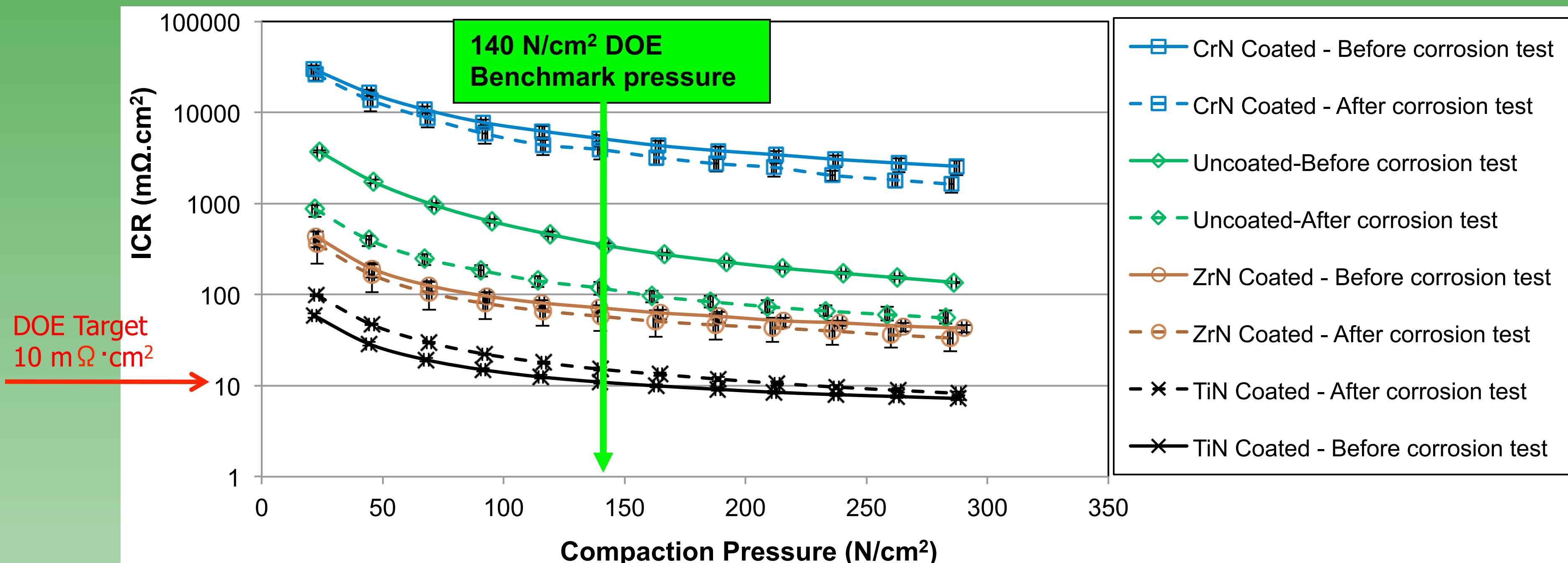
Davies et al. Journal of Applied Electrochemistry. 30 (2000) 101-105
Wang et al. J. Power Sources. 115 (2003) 243-251.

ICR of Coated BPPs



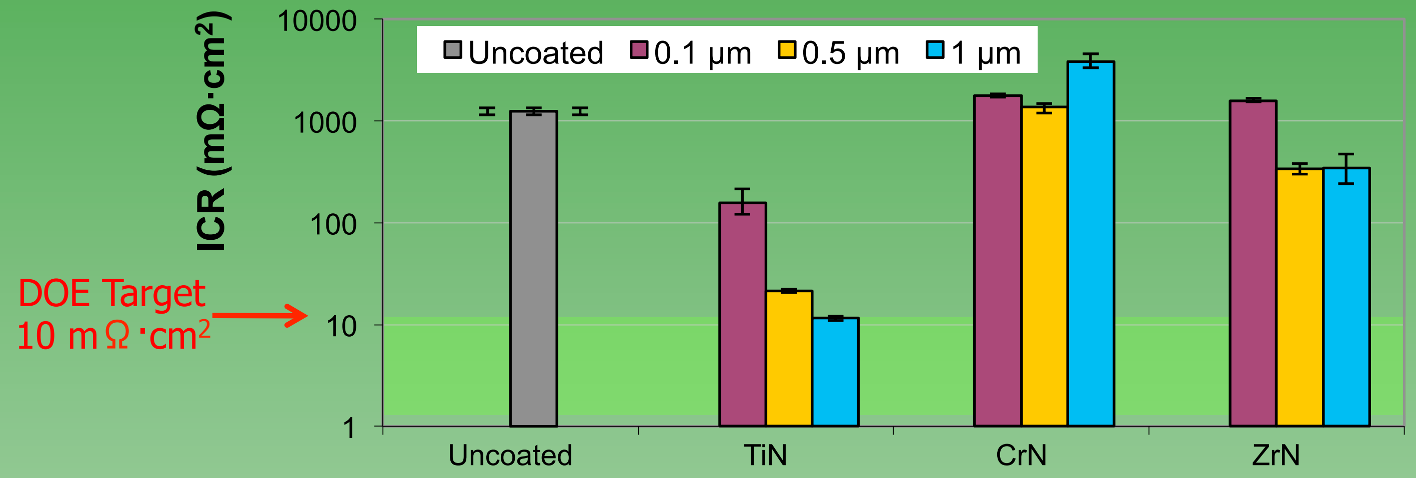
Coating Method: Physical vapor deposition (PVD)
Coating Materials: CrN, TiN, ZrN
Coating Thicknesses: 0.1, 0.5 and 1 um

ICR with Various Compaction Pressure



- ICR differences between various coating are distinct
- Exponential decrease with Compression pressure
- ICR decreases after corrosion test

ICR of Coated Blank Sheets

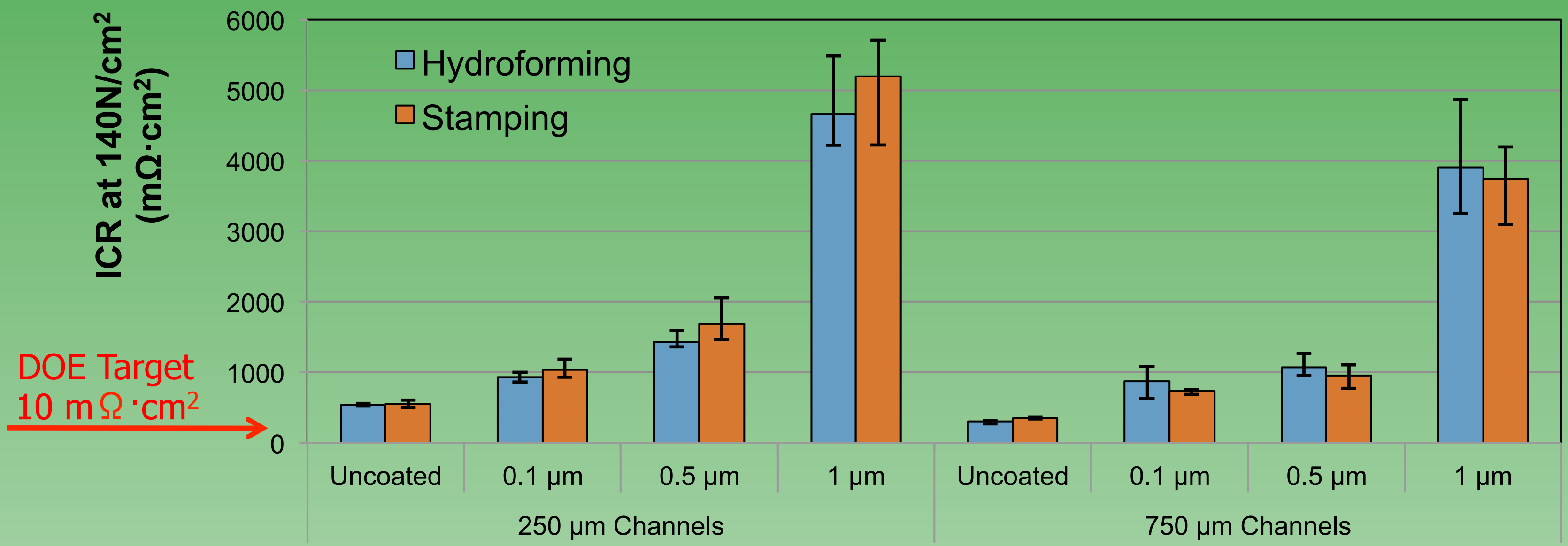


- Unformed
- Coated
- SS316L

Effect of coating material and thickness

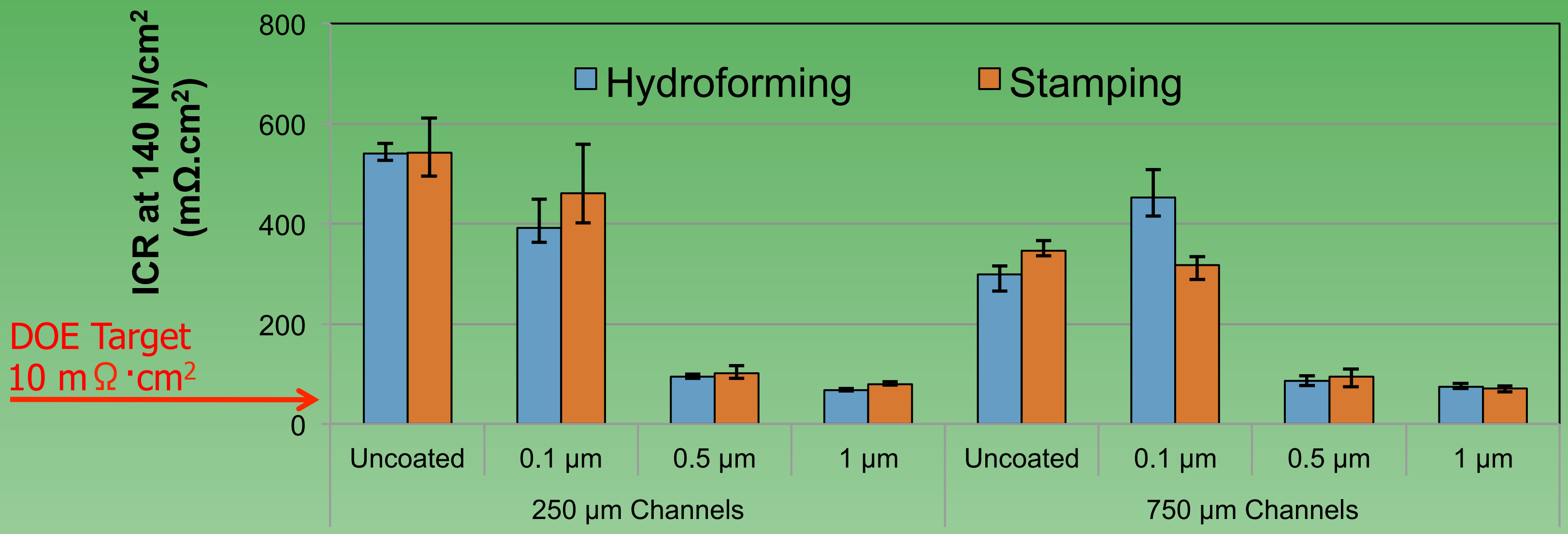
- Coating material is very effective on ICR
- TiN<ZrN<Uncoated<CrN
- Only TiN meets DOE target.
- Increasing CrN thickness increases ICR
- Increasing TiN, ZrN thicknesses decrease ICR
- No significant difference between 0.5 and 1 µm ZrN (ANOVA)

ICR of CrN Coated BPPs



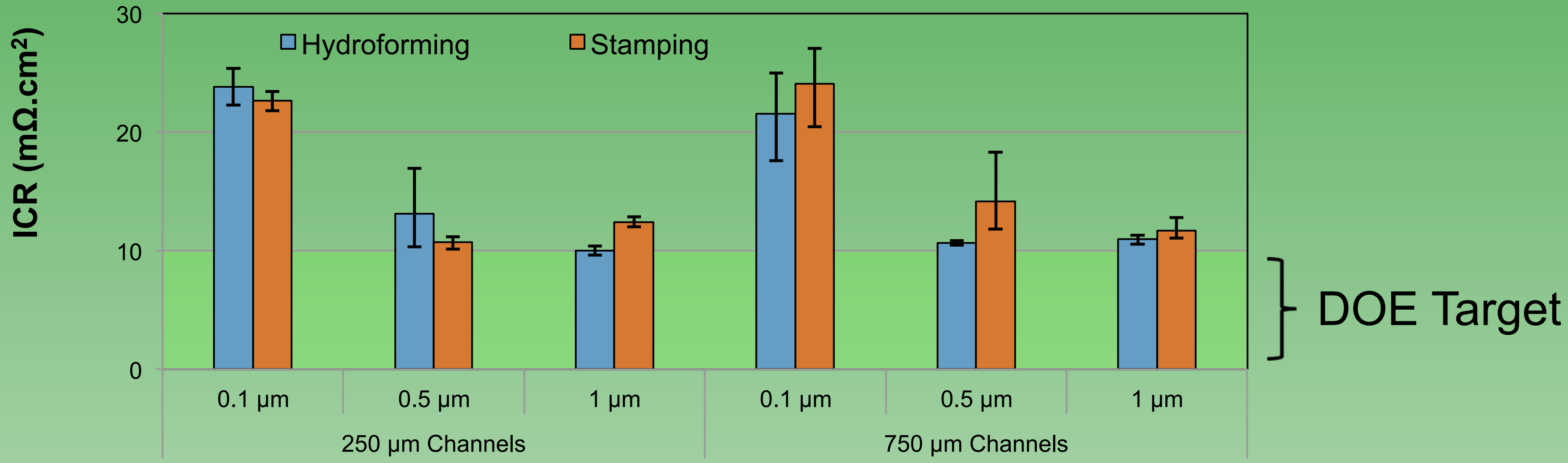
- **CrN coating increases ICR**
- Thicker coating layer gives higher ICR
- Difference between hydroforming and stamping is insignificant
- ICR values of CrN coated BPPs are too high for PEMFC.

ICR of ZrN Coated BPPs



- **ZrN coating decreases ICR**
- 0.1 µm coating thickness gives similar ICR to uncoated BPPs
- ICR of 0.5 µm ~ ICR of 1µm
- No significant ICR difference between hydroforming and stamping (ANOVA).
- ICR values of ZrN coated BPPs do not meet DOE target

ICR of TiN Coated BPPs



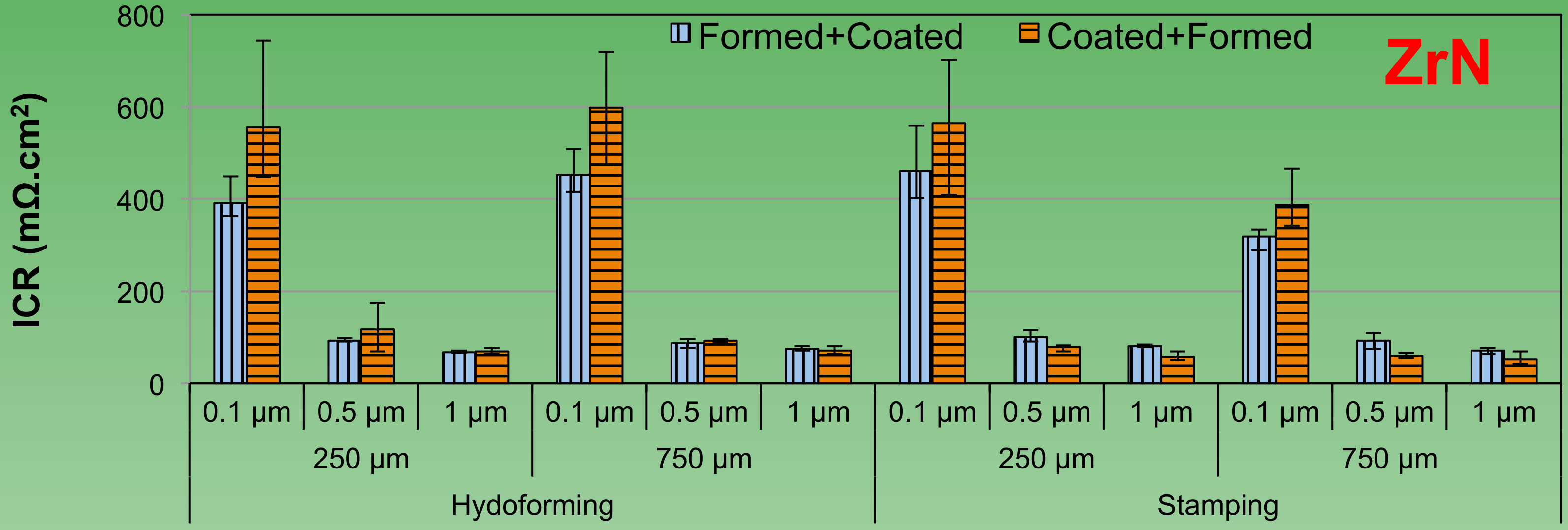
- **TiN coating significantly decreases ICR**
- ICR of 0.5 µm and 1µm similar
- Difference between hydroforming and stamping is insignificant.
- ICR values of 0.5 and 1 µm TiN coated BPPs are around DOE target

Effect of Process Sequence on ICR

Process Sequence	Advantages	Disadvantages
Forming Then Coating	Intact coating layer	Discrete production High cost Slow manufacturing rate
Coating Then Forming	Continuous production Low cost High manufacturing rate	Possible defect on coating layer

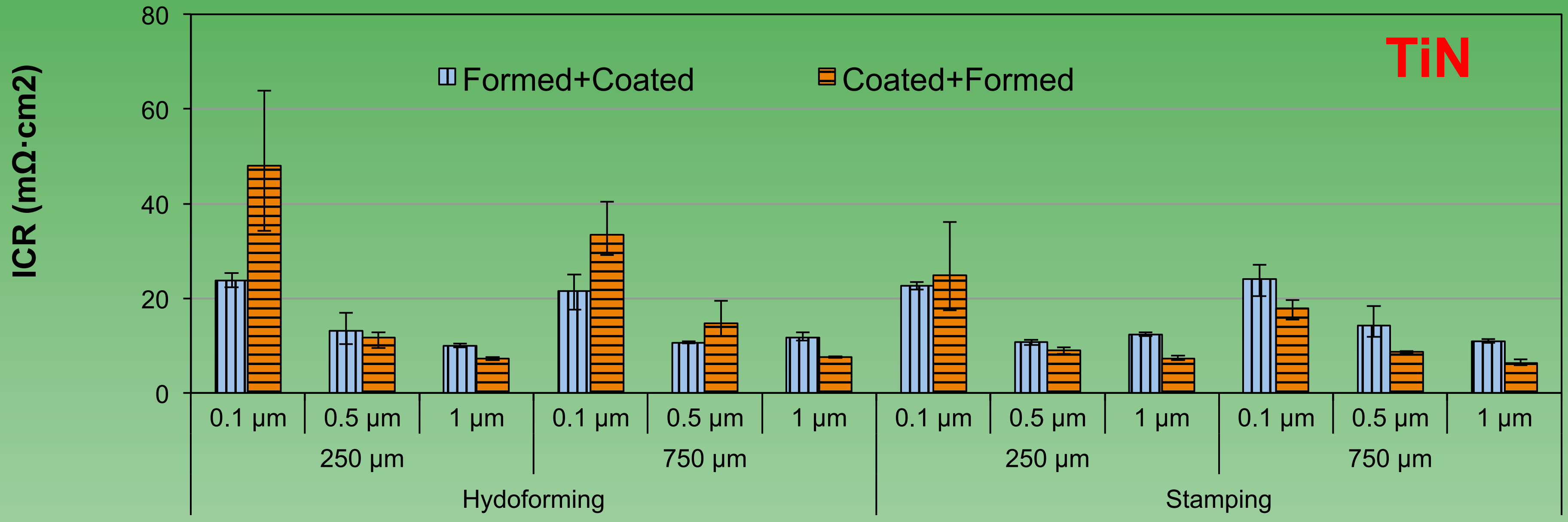
Picture:www.sandvik.com

Effect of Process Sequence on ICR



- No statistically significant difference in 0.1 µm due to variations
- **Coated+Formed is better in 0.5 and 1 µm**
- ICR values of ZrN coated BPPs are higher than DOE target

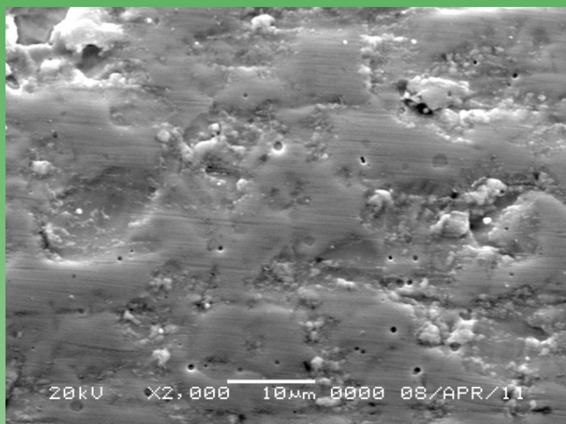
Effect of Process Sequence on ICR



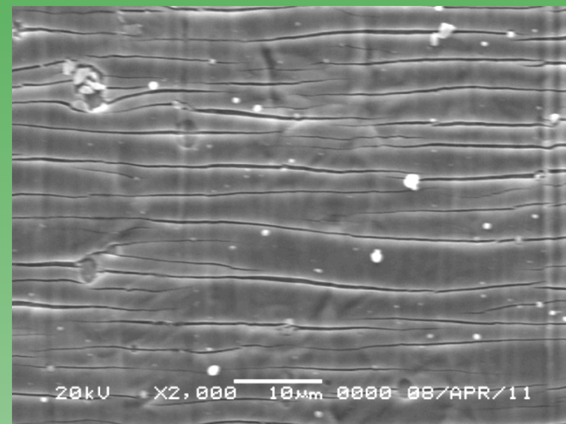
- **Similar or better ICR performance of “Coated Then Formed” compared to “Formed Then Coated” BPPs**

SEM images of TiN coated BPPs

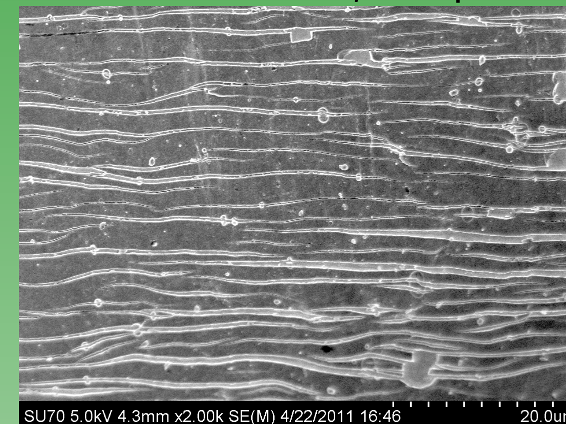
Formed+Coated, 1 µm



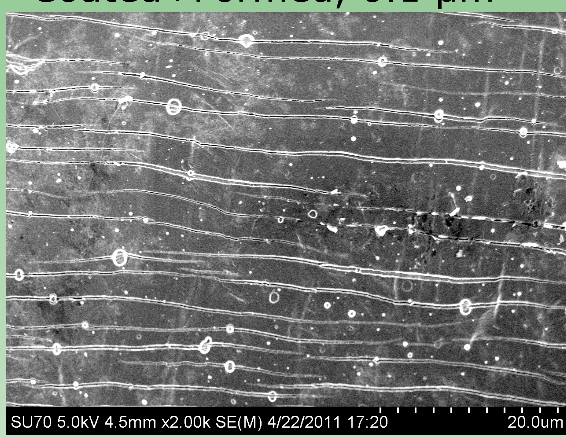
Coated+Formed, 1 µm



Coated+formed, 0.5 µm

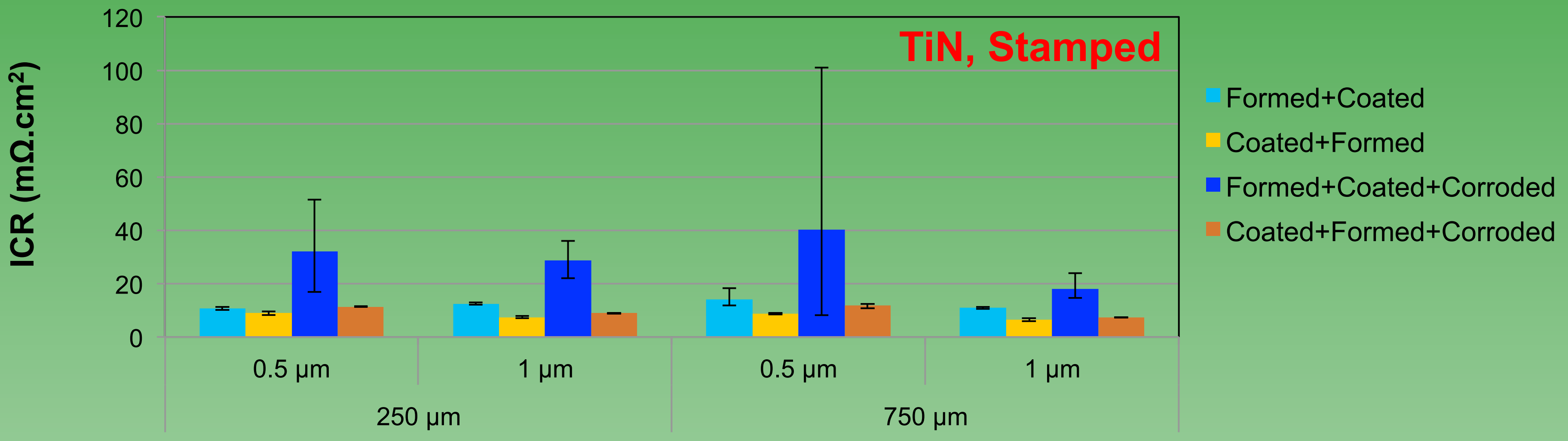


Coated+Formed, 0.1 µm



- Coating pits on formed then coated BPPs
  - Cracks parallel to channels on coated then formed BPPs

Effect of Corrosion Test on ICR



- **ICR increased after corrosion test**
- **Thicker coating is more stable against corrosive conditions**

Conclusions

Uncoated Samples

- The channel size and hydroforming pressure by modifying contact geometry was found to be significant factors on ICR.
- Stamping and hydroforming did not yield any certain pattern in most cases.
- **Do not meet DOE target level.**

Coated Samples

- Effect of coating and coating thickness were the most significant effecting parameters.
- Effect of manufacturing method and die geometry were insignificant.
- **Stamping with high punch speeds seem more appropriate for mass manufacturing of metallic BPP.**
- **Coating before forming looks promising and is worthy for further investigation.**

Acknowledgments

- NSF I/UCRC Program (Center for Precision Forming-CPF and its industrial members under NSF IIP Grant #: 0638588)

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- Ph.D graduates
    - Dr. Omer N Cora, Karadeniz Tech Univ, Turkey
    - Dr. Sasawat Mahabunphachai, MTEC, Thailand
    - Dr. Ender Dur, IGDAS, Turkey
    - Dr. Cabir Turan, IGDAS, Turkey
    - Dr. M. Fatih Peker, VCU, USA

Related Publications

- MF Peker, ON Cora, **M Koç**, (2011), 'Investigations on the Variation of Corrosion and Contact Resistance Characteristics of Metallic Bipolar Plates Manufactured under Long-run Conditions', *International Journal of Hydrogen Energy, doi:10.1016/j.ijhydene. 2011.08.067*

- C Turan, ON Cora, **M Koç**, (2011), 'Effect of Manufacturing Processes on Contact Resistance Characteristics of Metallic Bipolar Plates in PEM Fuel Cells', *International Journal of Hydrogen Energy, v36, n19, September 2011, Pages 12370-12380*

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