Business from technology

Screening of plasma nitrided CrN coatings for PEMFC bipolar plate

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Outline

Introduction

- The scope of this study
- Different Cr manufacturing methods
- Plasma nitridation

Measurement methods and equipment

- Multisinglecell
- Test procedure

Results

- Corrosion product analysis
- ICR
- Water contact angle

Summary

VTT Technical Research Centre of Finland

- Globally networked multi-technological contract research organization
- Provides high-end technology solutions and innovation services
- Turnover: 280 M€ (budget for 2010)
- Personnel: app. 3200, 78% with higher academic degree
- Fuel cell team
  - Focus mainly on PEMFC, SOFC and enzyme catalyzed and printed fuel cell technologies
  - Mainly system level and materials research
  - Personnel: 30

Scope of the study

- Base material stainless steel for PEMFC bipolar plates
- Protective coatings necessary
- Nitride coatings seem feasible
  - CrN, TiN the most promising

- In this study:
  - A coating for SS316L by a hard Cr layer which is subsequently plasma nitrided → CrN protective layer
  - Study includes 3 different manufacturing methods for Cr tested in a multisinglecell
  - Contact resistance before and after test
  - Corrosion product content of MEA and GDL
  - Water contact angle of the coating surface

Different methods to manufacture CrN

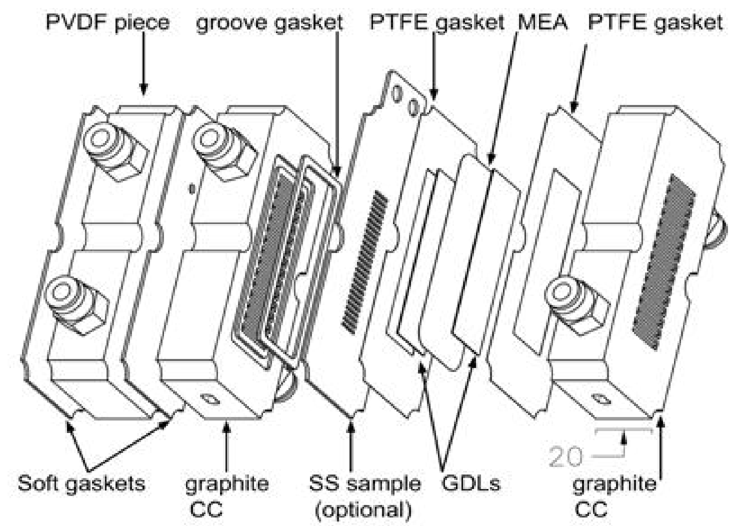
- PVD Cr
  - Well known method to produce thin hard layers
  - Can suffer from microcracks or other defects
- Electroplated hexavalent Cr
  - Industrial process, mass production available
  - Hazardous to health
- Electroplated trivalent Cr
  - In-house method, no industrial process available
  - A few candidates based on chlorides or sulfates
  - More complicated than hexavalent process
- Plasma nitridation
  - Nitrogen in ionized state
  - Temperature can be decreased (vs. thermal nitridation), range 200-600 °C

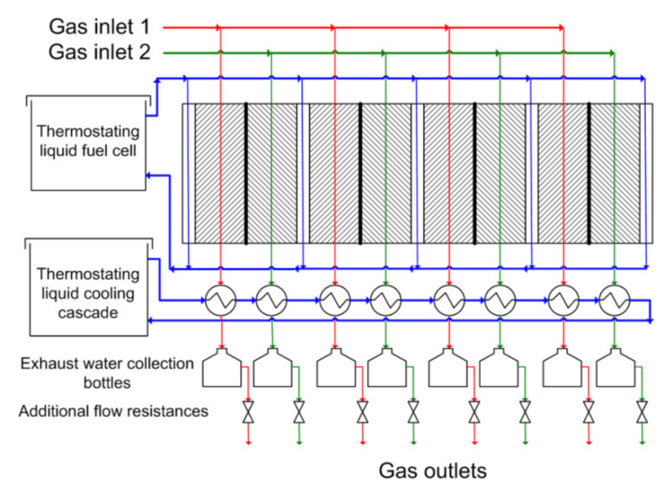
Stainless steel sample tested in the fuel cell

Multisinglecell

- Multisinglecell resembles a stack with some differences
  - Cells are electrically insulated, connections in parallel or in series
  - Cell outlets are separated → collecting exhaust water possible
  - Gas splitting can be done internally or externally
  - Thermostating liquid flowing between cells → same temperature

Test station capacity multiplied
Good screening tool





Test procedure

- An 8-cell setup of the multisinglecell was used
- 6 sample cells, 2 cells for reference
- Samples on the cathode
- 650 h test duration
- High temperature (80 °C)
- Fully humidified gases
- High stoichiometries
- Low current density

Samples tested in the multisinglecell

Cr layer type	Thicknesses
PVD	50 nm
	500 nm
	1 µm
Hexavalent	2 µm
	5 µm
	10 µm
Trivalent	10 µm

Corrosion product analysis

- PEMFC has acidic conditions

  → dissolution of corrosion products from the steel if protective coating not good enough
- After the test MEAs and GDLs were dissolved in an acid solution which was analysed for iron and chromium
- Iron is generally considered harmful for MEA
- All cations can cause decrease in MEA conductivity

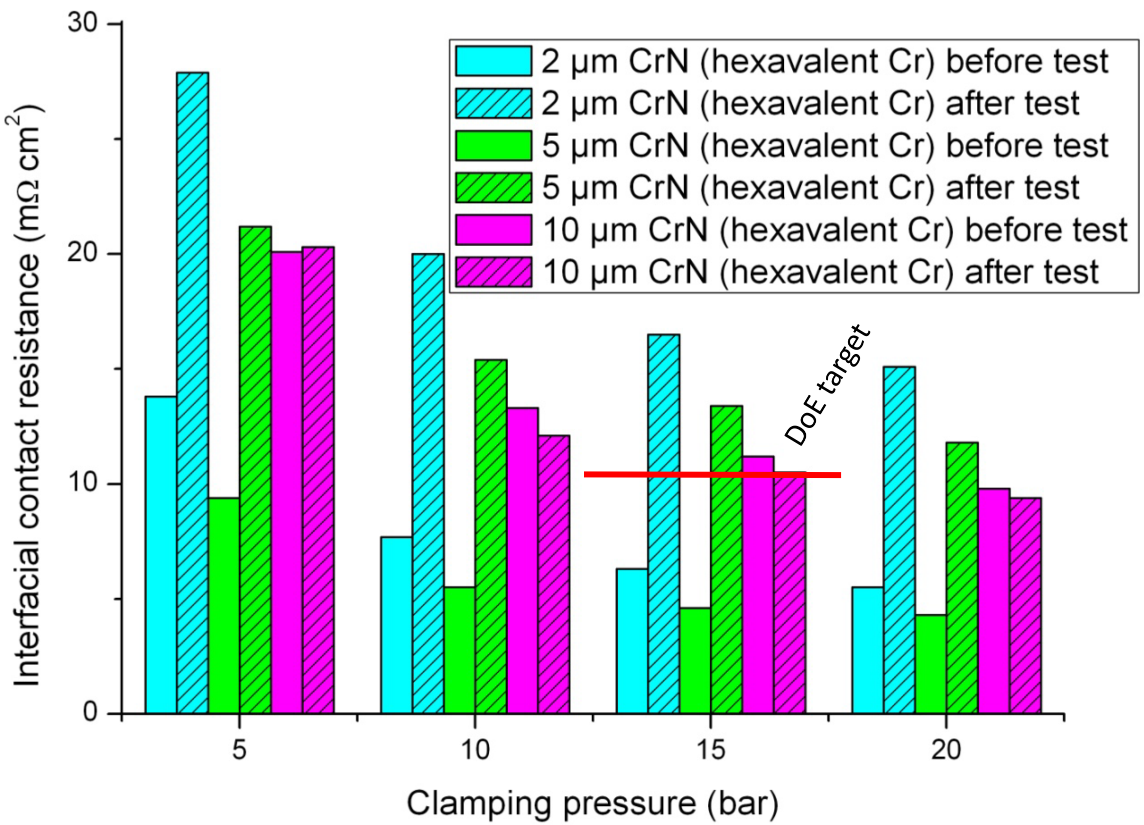
- Iron was found from some sample cells in significant amounts
- Chromium releases mostly very low

Iron release analysis

Sample	Minimum (µg)	Maximum (µg)
Reference	0.5	2
PVD 50 nm	0.5	27.4
PVD 500 nm	5.1	6.1
PVD 1 µm	4.1	10.1
Hex 2 µm	17.7	137.3
Hex 5 µm	2.1	5.3
Hex 10 µm	1.9	7.7
Tri 10 µm	0.6	4.9

- Most samples have good results
- Possibly the thinnest samples too thin
  - 20 µg of **Cr** release from the highest iron emitting 2 µm hex-Cr!
- Several hundreds of µg / 10 cm^2 adsorbed iron in MEA from severely corroded samples (previous study)

Interfacial contact resistance



- Trivalent CrN values varied between 10 (cathode sample) – 65 (anode sample) mΩ cm^2
  - Variance in the quality
  - Lower ICR possible with development of the process ?
- PVD manufactured samples values in between Hex-CrN and Tri-CrN

Water contact angle

- Unclarity of the preference of hydrophobic or hydrophilic bipolar plate surface

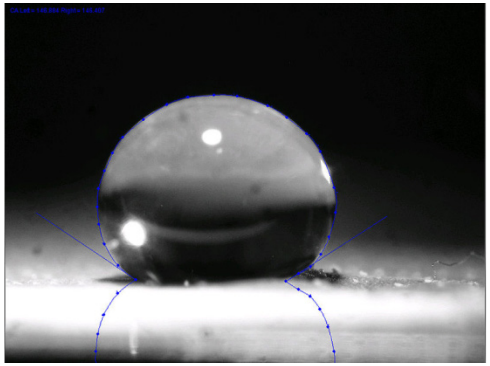
Hydrophobic surfaces:	Hydrophilic surfaces:
Ease the water removal from channels	Ease the water removal from the GDL and electrodes

Which is more beneficial?

→ Hypothesis: The stability of the surface characteristics is important!

Water contact angle

- The water contact angle was measured before and after fuel cell test



Sample	CA before	CA after
PVD CrN 50 and 500 nm	100°	Non-stable droplet - 20°
PVD CrN 1 µm	100°	15°-40°
Hex-CrN 2 µm	70°	10°-35°
Hex-CrN 5 µm	70°	25°-50°
Hex-CrN 10 µm	65°	40°-55°
Trivalent CrN	55°	45° (anode samples) 30° (cathode samples)

- The most stable contact angle values were obtained from samples:
  - Trivalent CrN sample
  - Hex-Cr 10 µm

Summary

- In this study three different methods to produce CrN
  - Plasma nitridation was applied to
    - PVD Cr
    - Conventional electrodeposited hexavalent Cr
    - New electrodeposition process for trivalent Cr

- The iron release results were good for all but the thinnest CrN layers
- The ICR values varied
  - Best results from 5 μm and 10 μm hex-CrN
  - Trivalent CrN has potential for low ICR as well if process is developed

- Most stable contact angle with trivalent CrN and 10 μm hexavalent CrN

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Thank you for your attention!