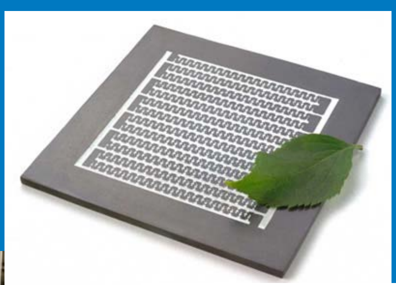
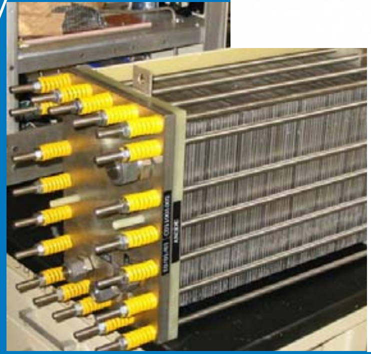
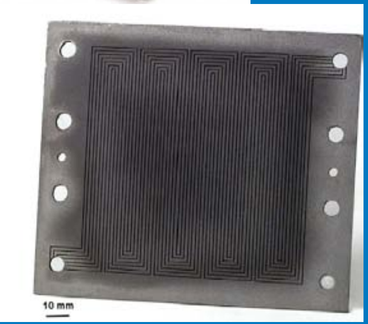
Modified Stainless Steels for PEMFC Bipolar Plates



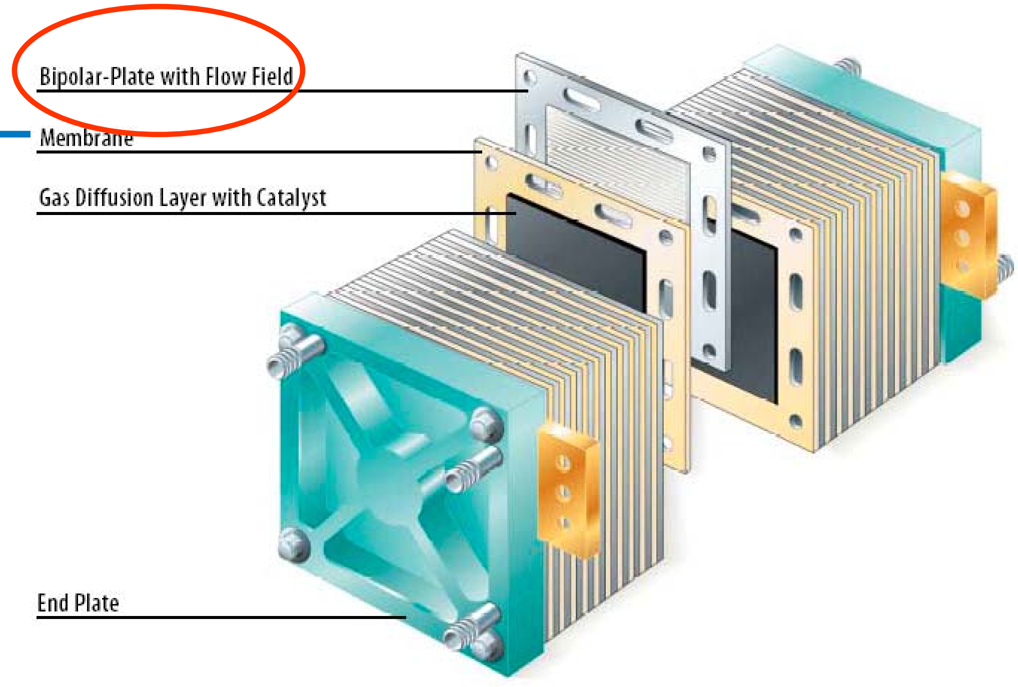




Heli Wang and *John A. Turner,*
National Renewable Energy Laboratory
Michael P. Brady,
Oak Ridge National Laboratory
April 16, 2012

Hydrogen – Bipolar plates for PEM fuel cells & electrolyzers

Outline



- **Advantages and Challenges**
- **Our Approach**
- **Bare Metals**
- **Surface Modification/Coatings**
  - SnO_2:F conductive coating
  - Thermal Nitridation (ORNL)
  - Plasma Nitridation
  - Electrochemical Nitridation

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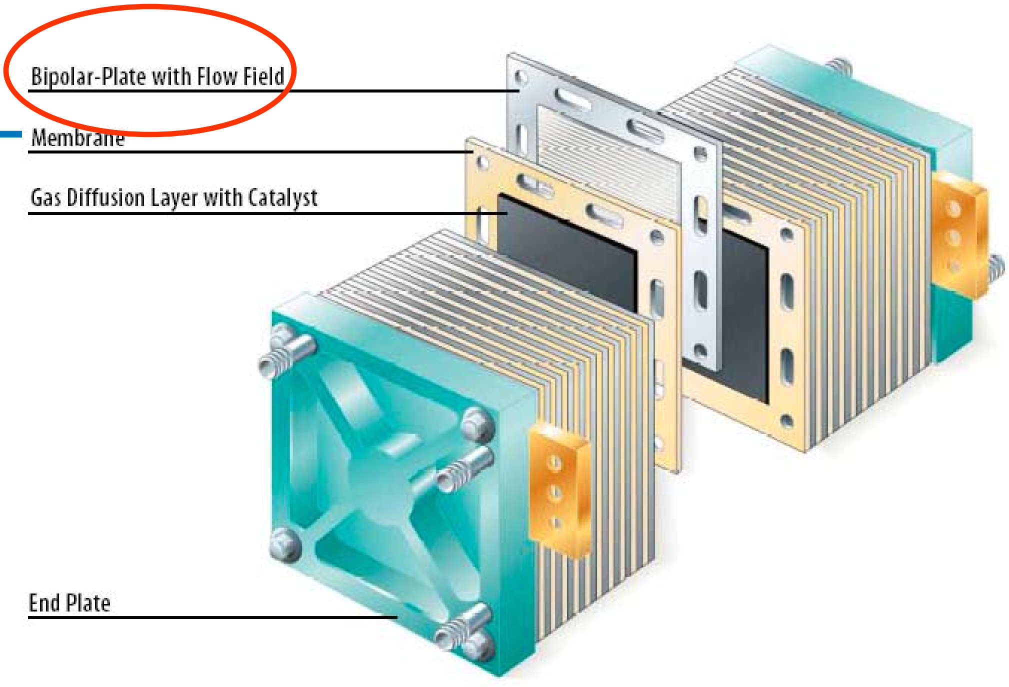


Advantages and challenges of Metallic BP

Advantages

- Replacement for currently used graphite plates
  - Brittle: thick (low stack power density),
  - Expensive to machine;
- Wide choices of alloys, low cost, high chemical/thermal stability, corrosion resistance;
- High strength allowing thin plates for high power density;
- High bulk electrical and thermal conductivity;
- Existing low cost/high-speed high-volume manufacturing pathway (e.g. stamping, embossing, rolling, etching…)

Challenges

- Higher ***surface contact resistance*** due to surface oxides (which provide excellent corrosion resistance); (cathode side)
- Possible contamination of membrane by dissolved metal ions from ***corrosion*** by-products. (anode side)

Our Approach

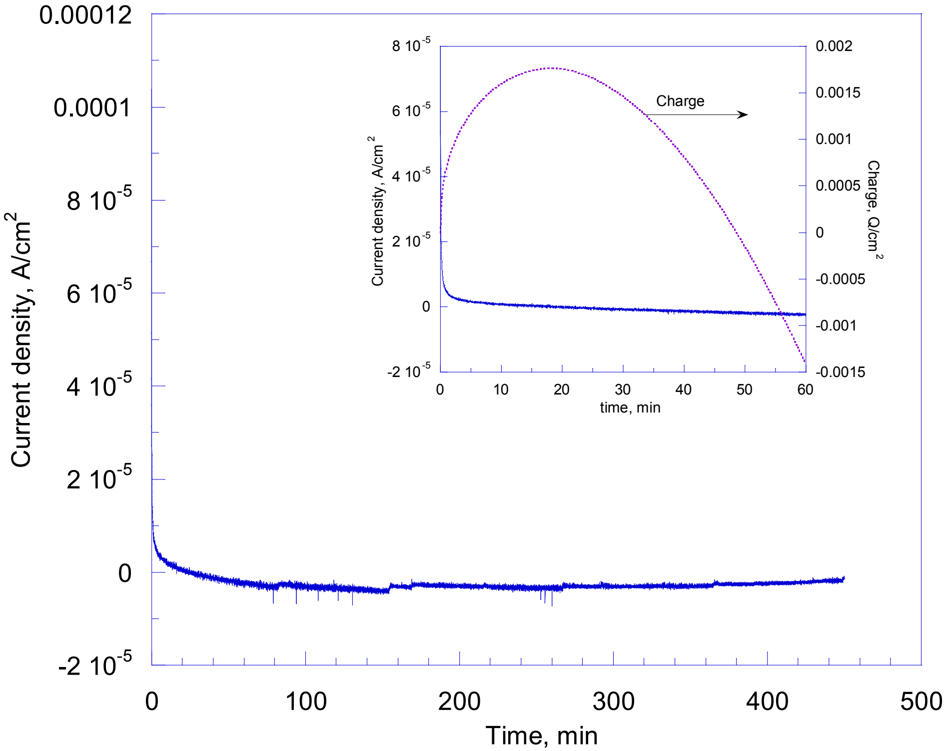
- Understanding alloy composition vs. bipolar plate performance relationship; **(Substrate)**
- Study possible coating materials and surface modification preparations and methods;
- Modify the surface conductivity with the alloys that have good corrosion resistance in PEMFC environments;
- Develop suitable Substrates/surface modification (coatings) processes to meet the DOE targets (2011 updated):

DOE 2017 cost goal: $3/kW
Resistivity: 0.01 Ohm·cm^2
Corrosion rate: < 1 μA/cm^2

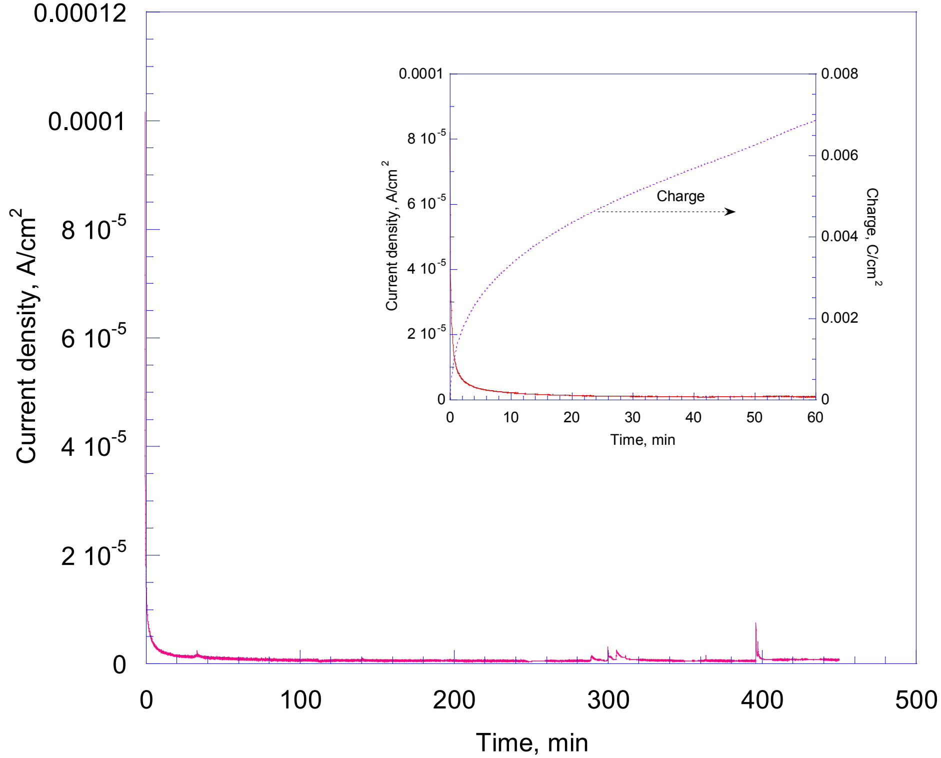
Bare steels in PEMFC environments

Example: Type 349TM

PEMFC anode
~ -1 μA/cm2

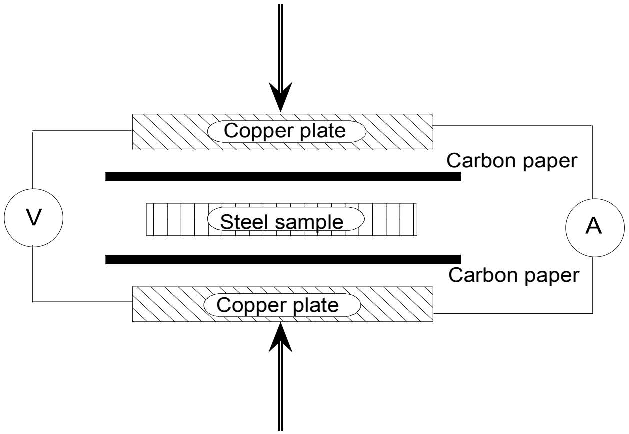


PEMFC cathode
0.3~0.6μA/cm2



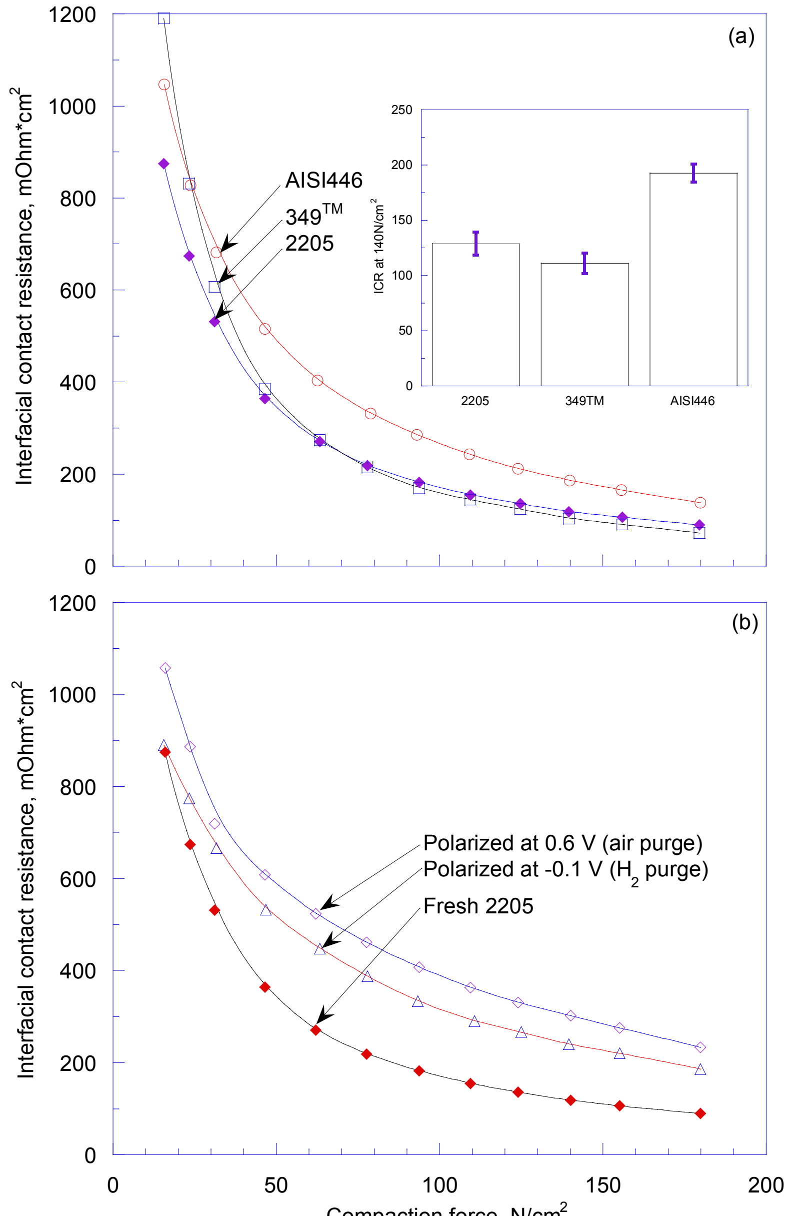
Heli Wang, Mary Ann Sweikart, John A. Turner, *J. Power Sources* **115** (2003) 243-251.

Interfacial contact resistance (ICR)



$$R = \frac{V \cdot A_S}{I}$$

J. Power Sources **115** (2003) 243-251.



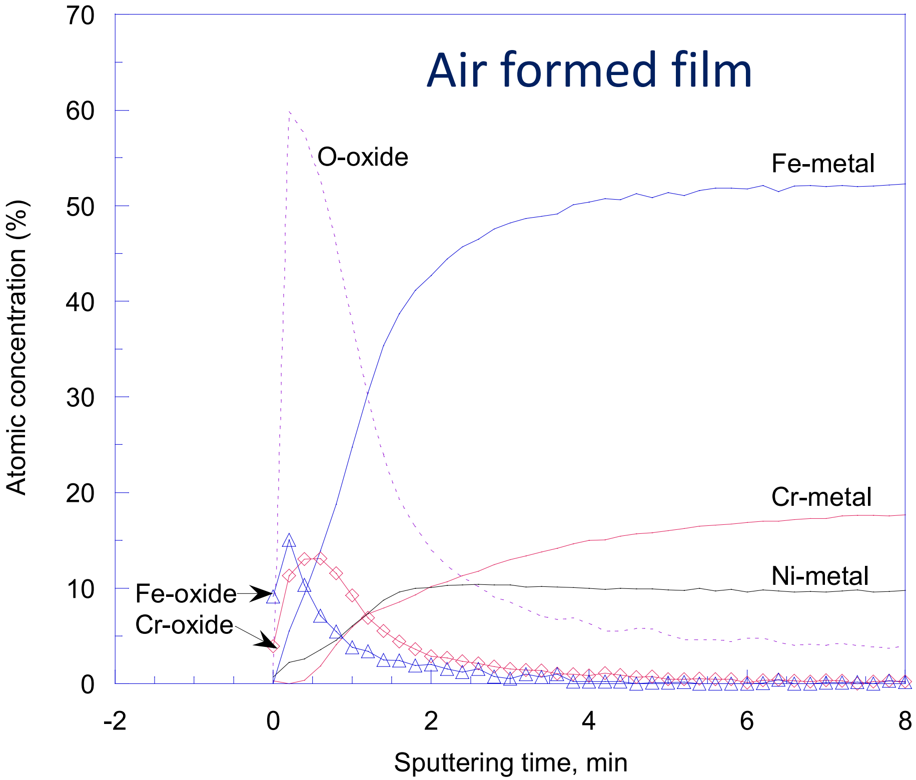
(a) ICR decreases with compaction force; ICR differs from different stainless steels; ICR of the steels at 140 N/cm^2 , i.e. approximately 130 mOhm·cm^2 for 2205, ~110 mOhm·cm^2 for 349^{TM}, and ~190 mOhm·cm^2 for AISI446;

(a) Passivation (passive film) affects the ICR. **ICR increases after polarization.**

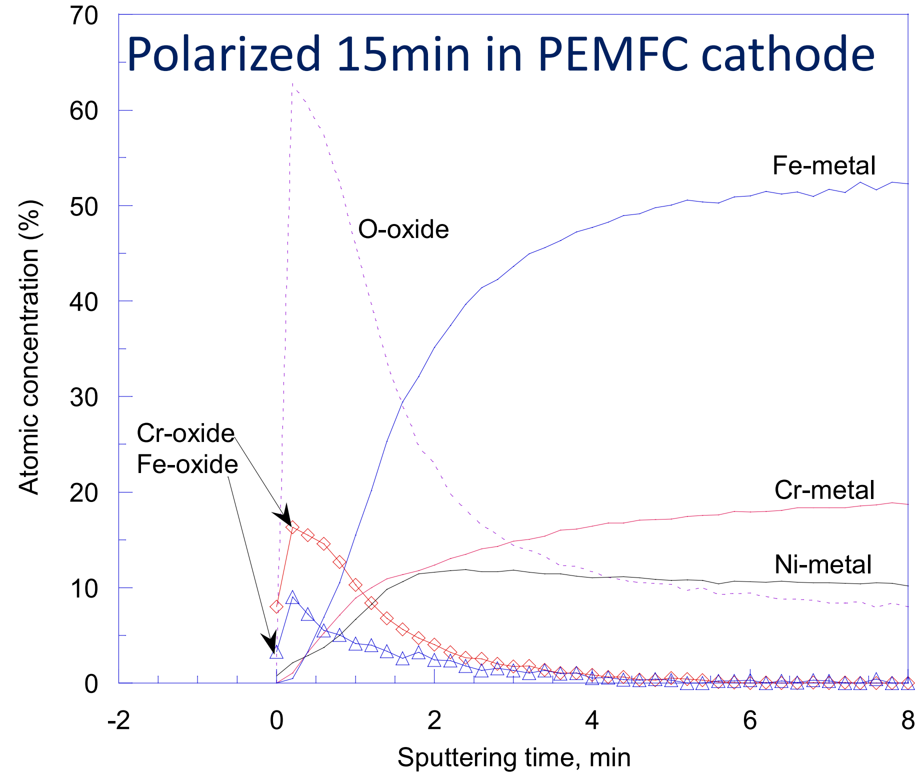
J. Electrochem. Soc. **152** (2005) B99.

High ICR is related to surface/passive films

XPS depth profile for 349™ steels



Mixed oxides



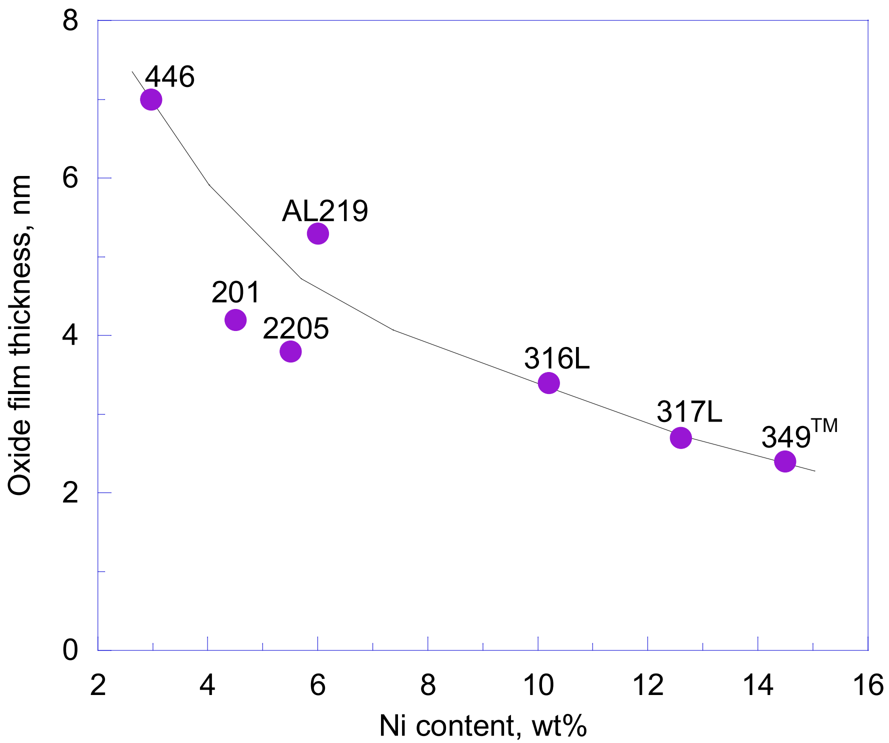
Cr-oxide dominates

Heli Wang and John A. Turner, *ECS Transactions*, 1(6), 263-272 (2006).

Summary Remarks (1)

- Tested over 20 bare metallic alloys (mainly stainless steels) in simulated PEMFC environments (Austenite, Ferrite, duplex, low-N);
- Some candidate steels showed very low corrosion rate; (DOE sub-target on corrosion rate was achieved);
- ICR with bare alloys still high;
- Passive films provided corrosion resistance, as well as the reason of high ICR;
- Ways to decrease ICR needed.

Oxide film thickness of steels



Dependency of air-formed oxide film thickness on the nickel content of stainless steels.

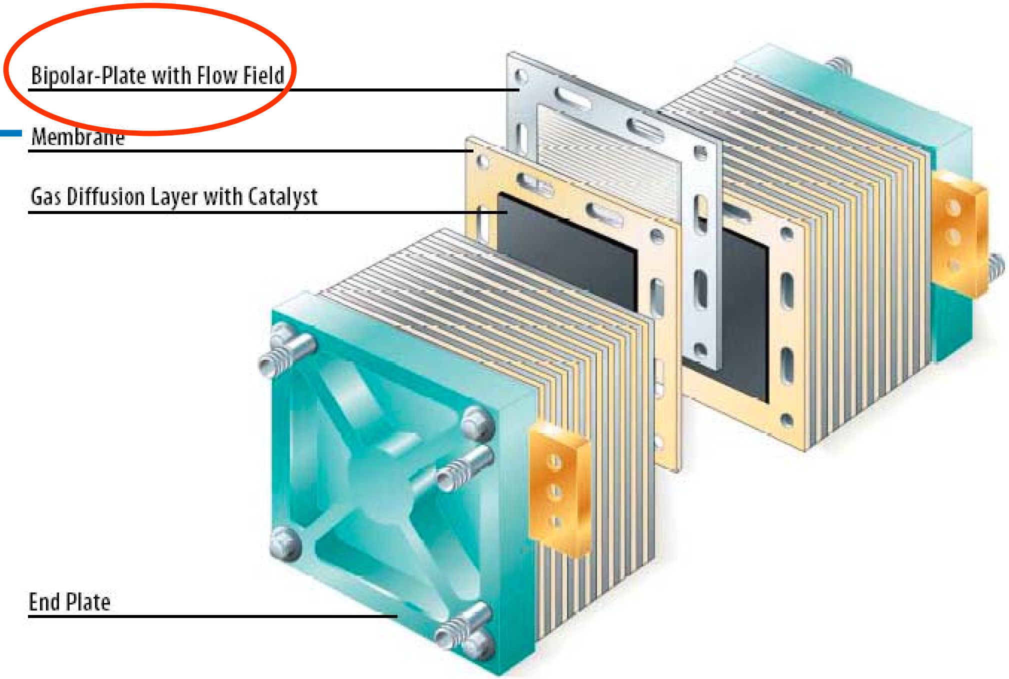
How to lowering the ICR?

Surface coating(s)/Modification (working on oxide film)

- SnO_2:F conductive coating
- Thermal Nitridation (ORNL)
- Plasma Nitridation
- Electrochemical Nitridation

Heli Wang, John A. Turner, *J. Power Sources* **180** (2008) 791-796.

Outline



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Conductive SnO_2:F Coating

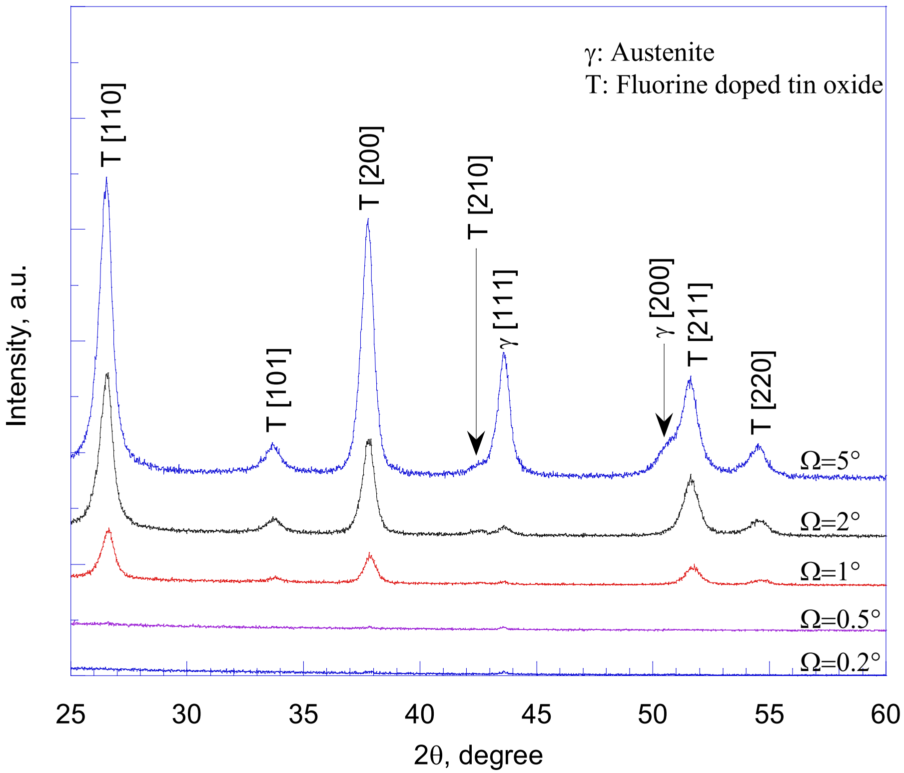
- **High conductivity----widely used in PV industry for long time;**
- **Volume production available;**
- **Offer appropriate protection in different environments;**
- **Reduce cost with lower grade alloys;**
- **NREL is unique in the techniques.**

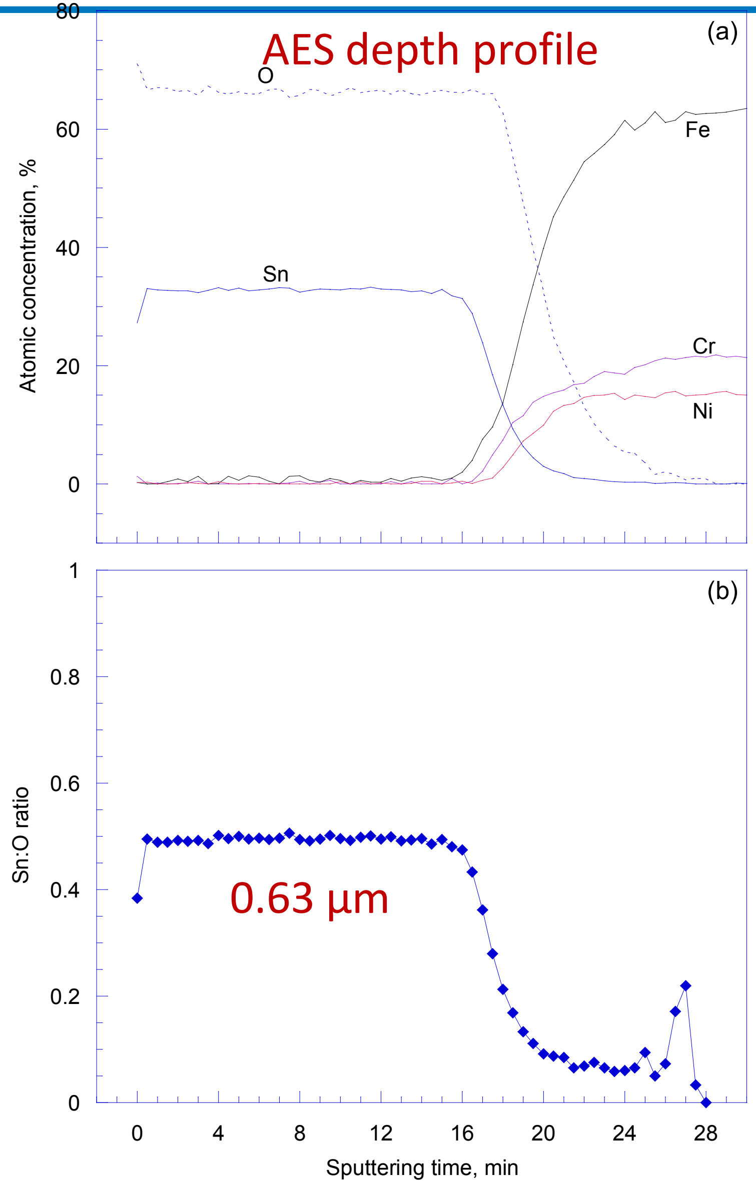
Procedure for “original” SnO_2:F coating:

- Low-pressure chemical vapor deposition (LPCVD) system
- UHP tetramethyltin and bromotrifluoromethane (CBrF3) used as the tin and fluorine precursors; UHP-grade oxygen used as the oxidizer.
- Chamber pressure kept at 6666 Pa (50 Torr) and deposition T was 550 C.
- A 0.6 µm (approximately) thick SnO_2:F film formed with a sheet resistance of 8 Ω/sq (a resistivity of 5 Ω-cm).

Characterization for Original SnO_2:F coated 349^{TM} steel

Typical glancing angle XRD patterns of the original SnO_2:F coated 349^{TM} steel

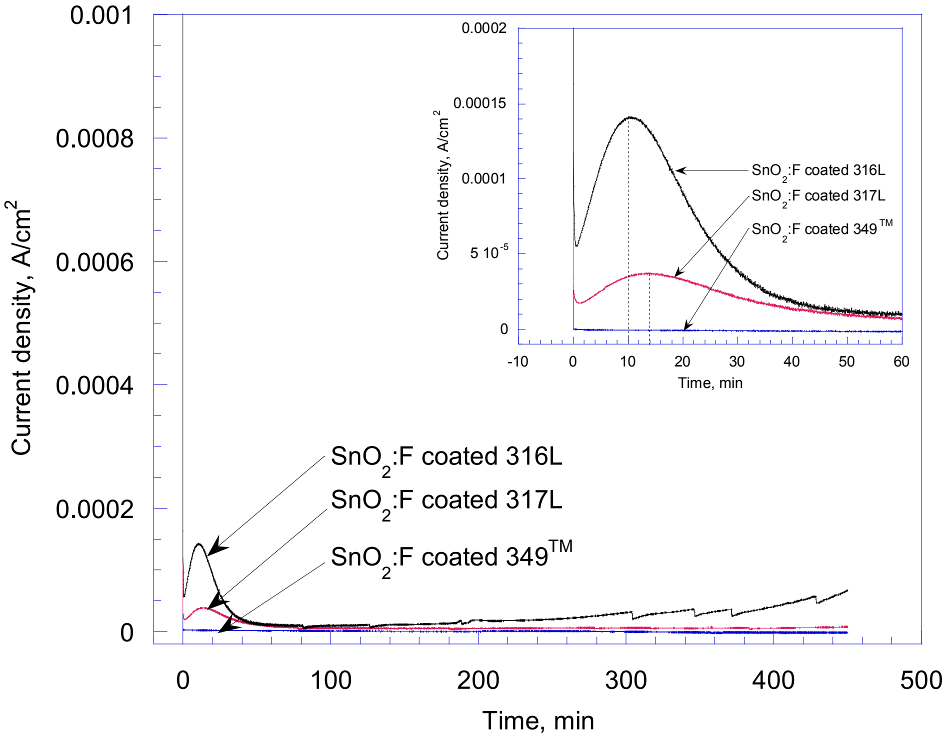




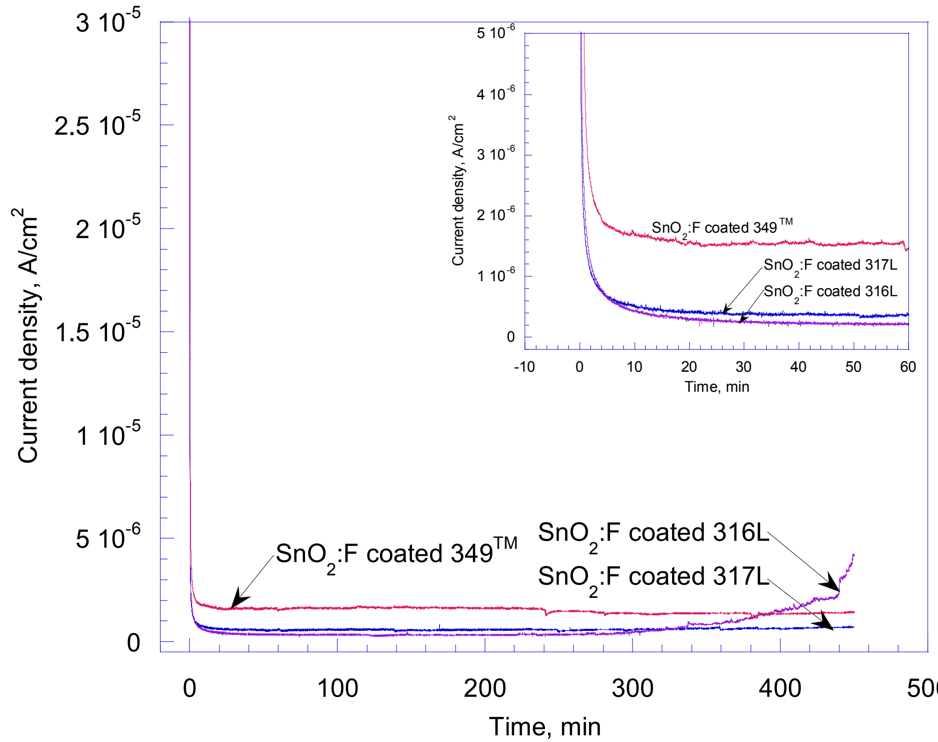
Heli Wang, John A. Turner, Xiaonan Li, Raghu Bhattacharya, *J. Power Sources* **171** (2007) 567.

Original coated 300 steels in PEMFC environments

PEMFC anode



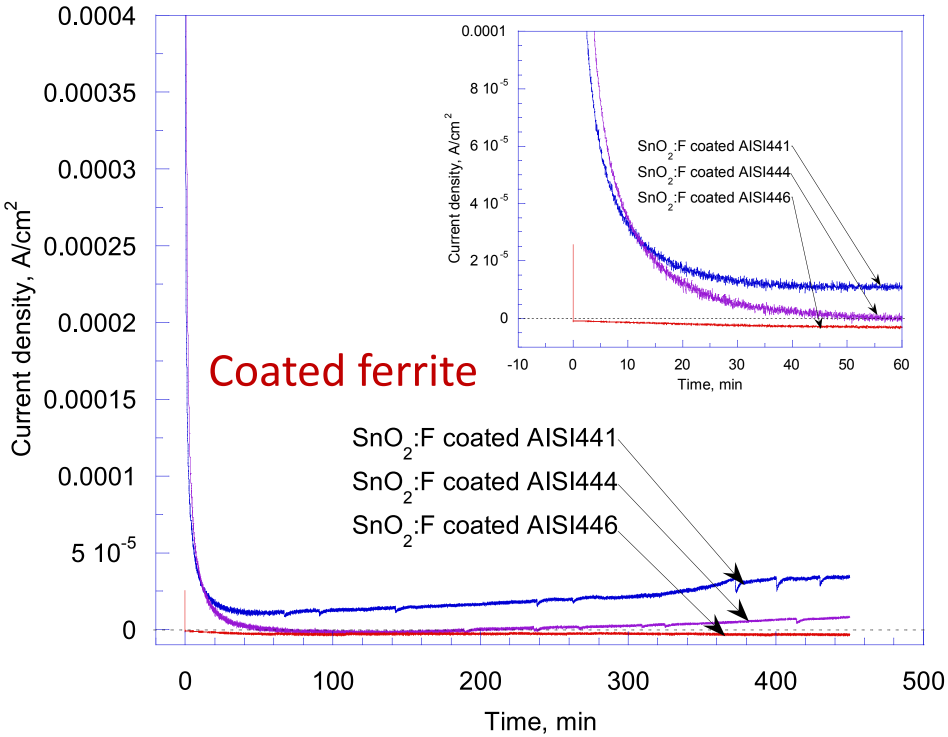
PEMFC cathode

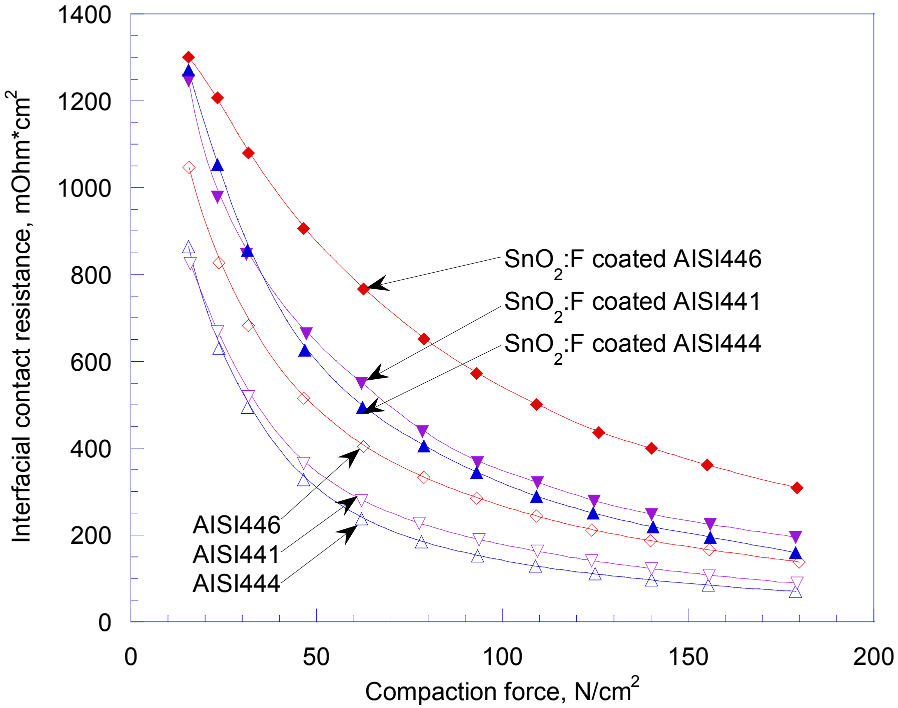


- Corrosion resistance of the coated steels is strongly related to substrate;
- Excellent behavior of SnO_2:F/349^{TM} expected;
- Current peaks for coated 316L (~140 μA/cm^2 at 10 min) and 317L (~35 μA/cm^2 at 14 min) in PEMFC anode environment.

Heli Wang, John A. Turner, Xiaonan Li, Raghu Bhattacharya, *J. Power Sources* **171** (2007) 567.

Original coated 400 steels in PEMFC anode environment

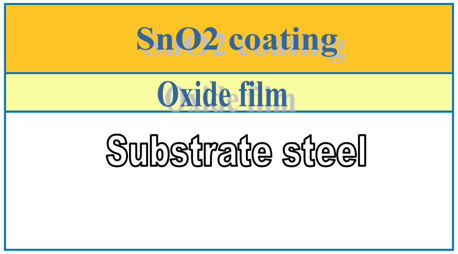




- Corrosion resistance of coated steels is strongly related to substrate;
- Excellent behavior of SnO_2:F/446 expected;
- Surprising good corrosion resistance of SnO_2:F/444.

However, original SnO_2:F coating ↑ ICR!

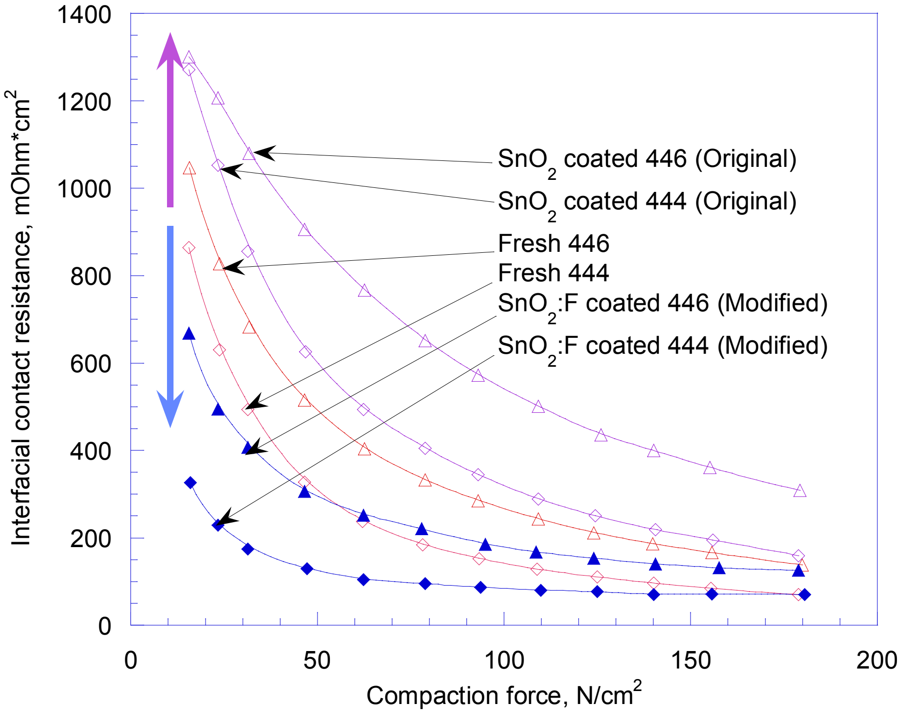
Original coated steels shifts the ICR (up) - just simply adding an additional resistance to the air-formed film.

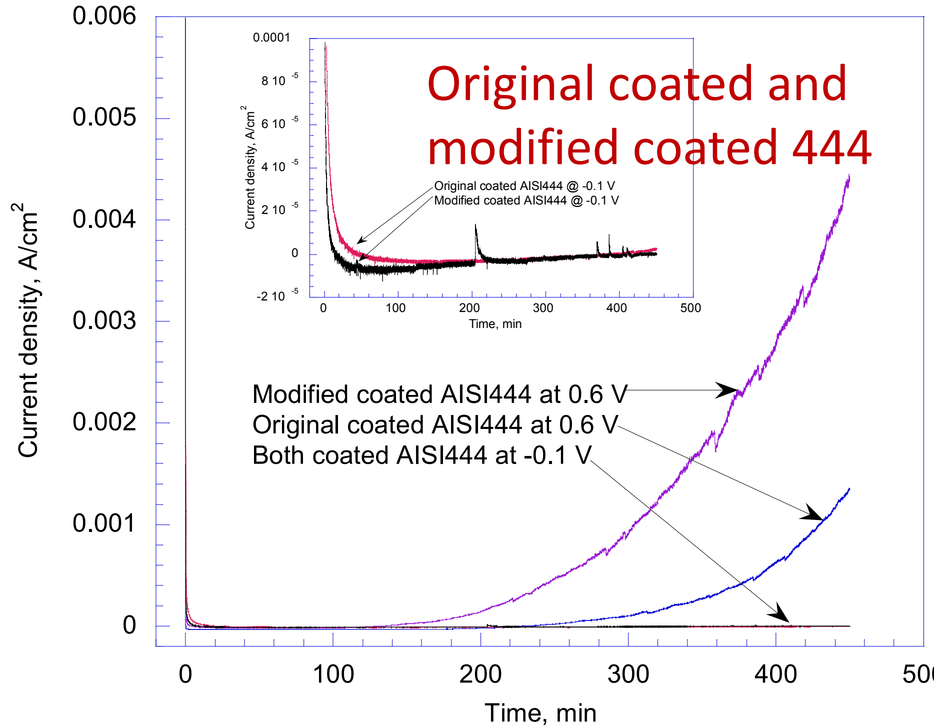


Heli Wang, and John A. Turner, *J. Power Sources* **170** (2007) 387.

Modifying the SnO_2:F coating for lower ICR

- Etch 0.3 to 4min with $CBrF_3$ into the chamber immediately before deposition to etch off some of the stainless steels' air-formed film;
- Poor adhesion for modified coating on austenitic and duplex steels samples as evidenced by surface wrinkles and peeling.
- Good coatings were only obtained with the ferritic stainless steels AISI444 and AISI446.





Coated 444: Similar behavior for coated 444 in PEMFC anode environment;

Poor behavior for modified coated 444 in PEMFC cathode environment;

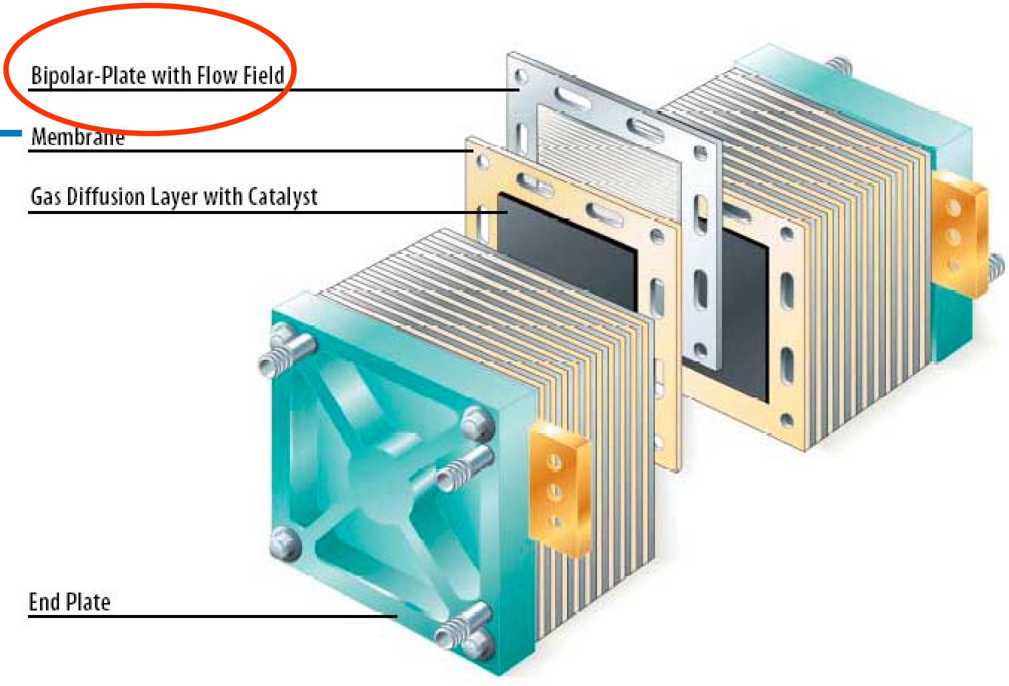
Coated 446: Original coated better than modified coated in PEMFC environments

Heli Wang, John A. Turner, Xiaonan Li, Glenn Teeter, *J. Power Sources* **178** (2008) 238.

Summary Remarks (2)

- Austenite (300), Ferrite (400) and Duplex (2205) steels were deposited with ~0.6 µm SnO_2:F coating.
- Behavior of original coated steels depends strongly on the substrates. In general, coated lower grade steels showed more improvement than that of coated higher grades.
- Adding a pre-etching process resulted in modified coating. Modified coated steels shifts the ICR ↓(down). However, modified coated steels (444 and 446) showed poorer corrosion resistance than the original coated ones.

Outline



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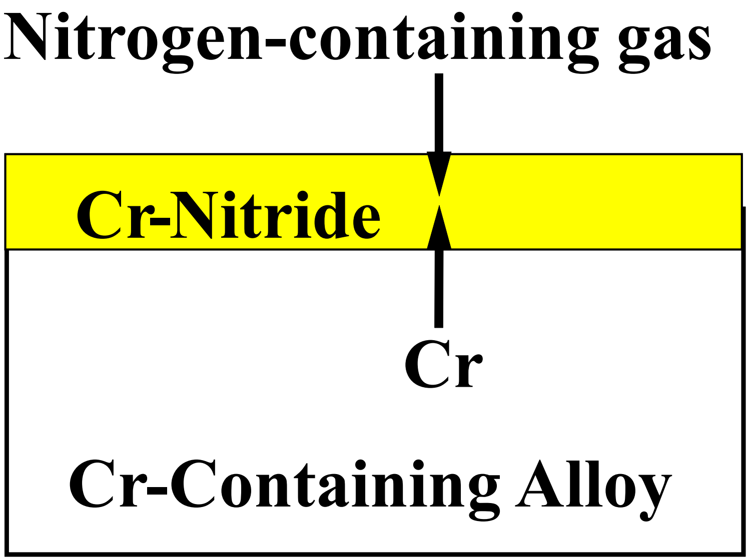
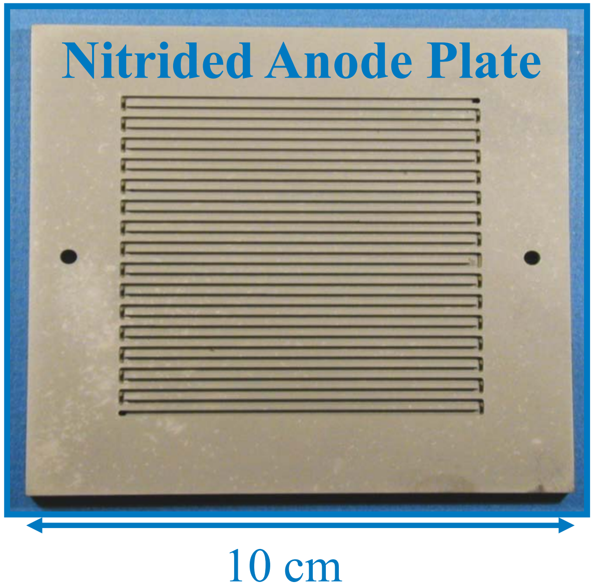
Thermal Nitridation – (ORNL: Brady/More)

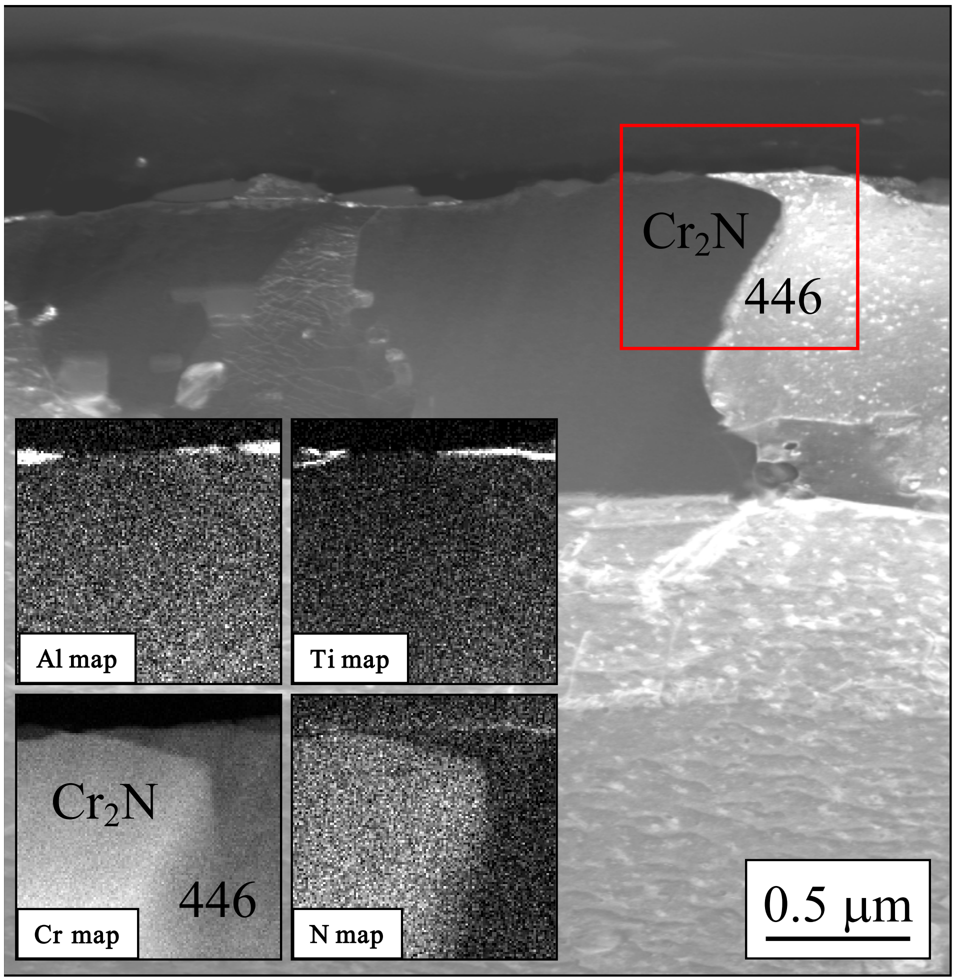
- **Surface conversion, not a deposited coating:**
- **High temperature favors reaction of all exposed metal surfaces**
  - Amenable to complex geometries (flow field grooves)
- **Stamp then nitride: Industrially established and cheap**



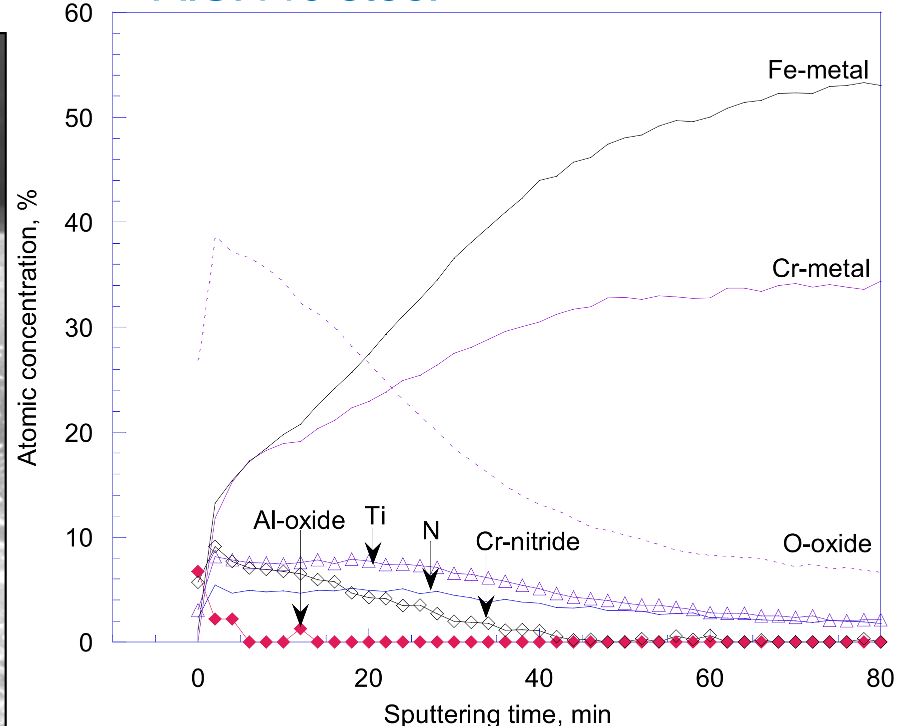


Fe-Cr Alloys Via "Nitrogen Modified Passive Oxide Layer"

TEM cross-section and elements mapping of 2h nitrided AISI446 steel



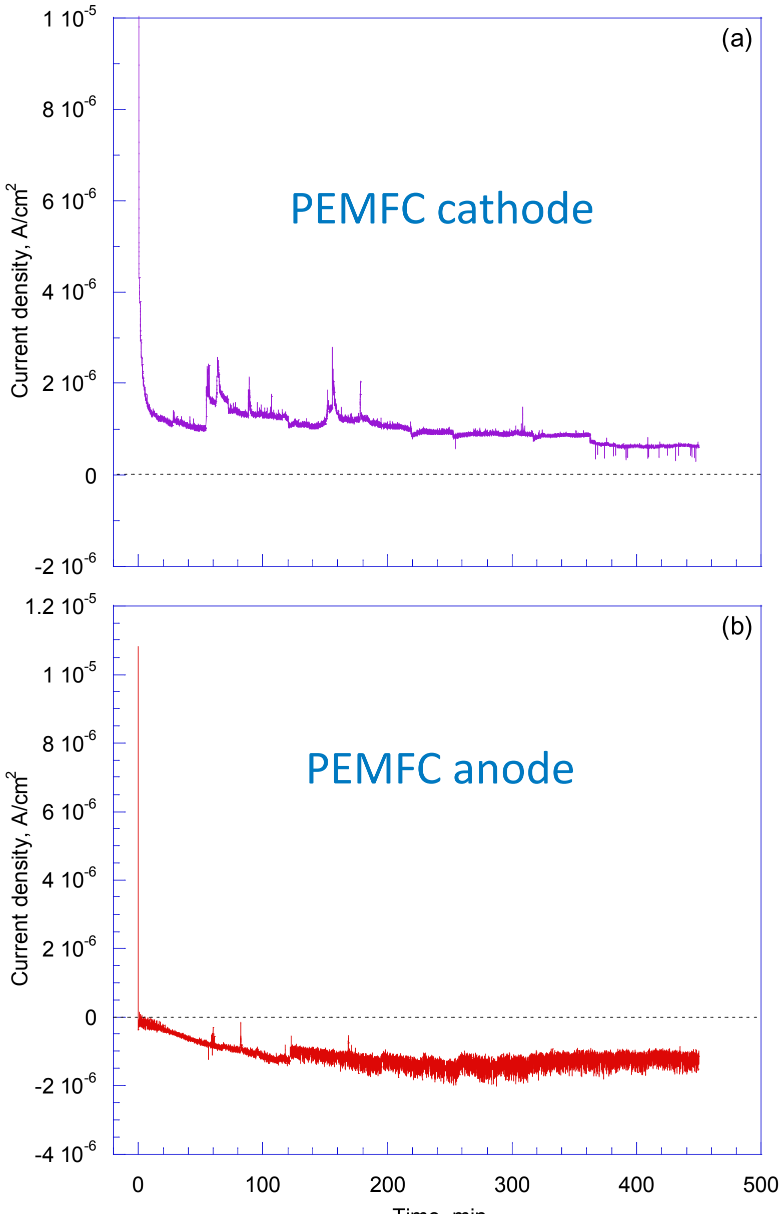
XPS depth profile of 2h nitrided AISI446 steel



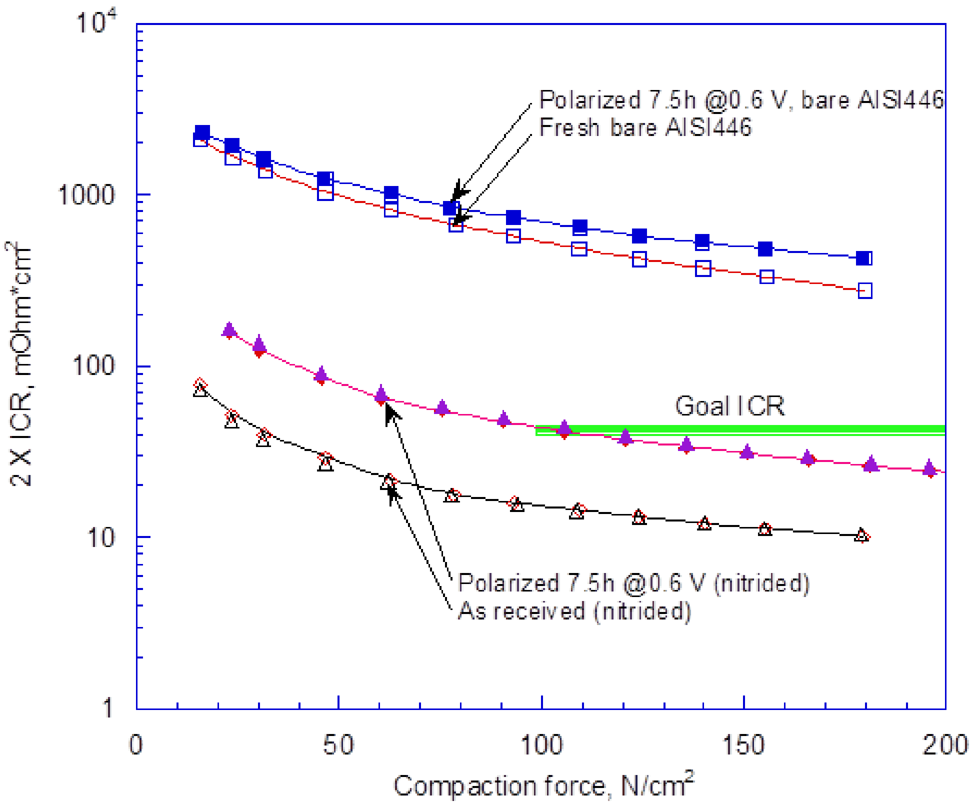
- Isolated Cr_2N grains and 10-100 nm thick Al-oxide/Ti-nitride surface (Cr_2N conductive path with "beefed" up passive layer)
- Surface complex oxygen-nitrogen mixture with Cr, Fe, other
  - **Not exclusive Cr-nitride surface like nitrided Ni-Cr**

H. Wang, M. P. Brady, K. L. More, H. M. Meyer III, J. A. Turner, *J. Power Sources* **138** (2004) 79.

Excellent corrosion resistance and low ICR for nitrided 446



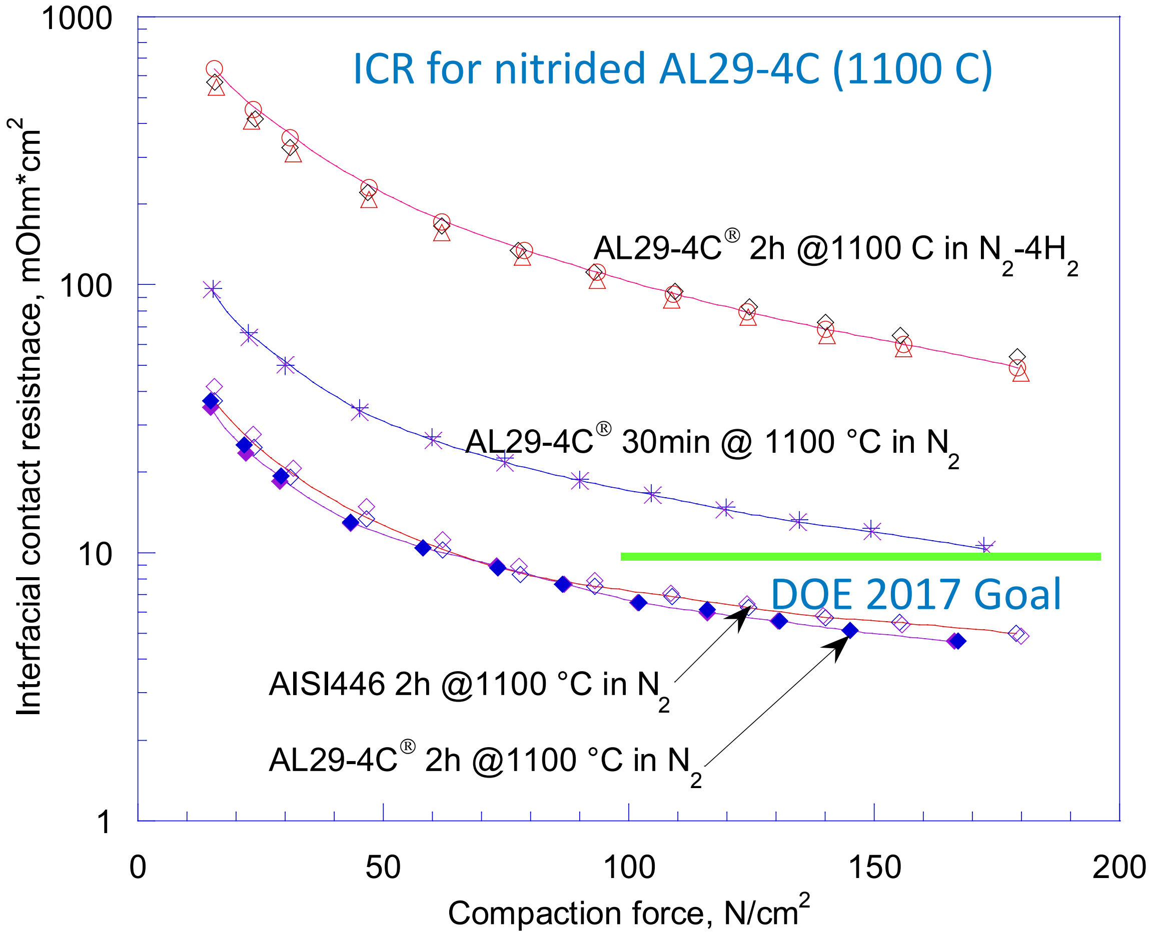
- **ICR significantly decreased, both as-nitrided and tested;**
- **Surface complex of oxygen-nitrogen mixture with Cr, Fe.**



H. Wang, M. P. Brady, K. L. More, H. M. Meyer III, J. A. Turner, *J. Power Sources* **138** (2004) 79.

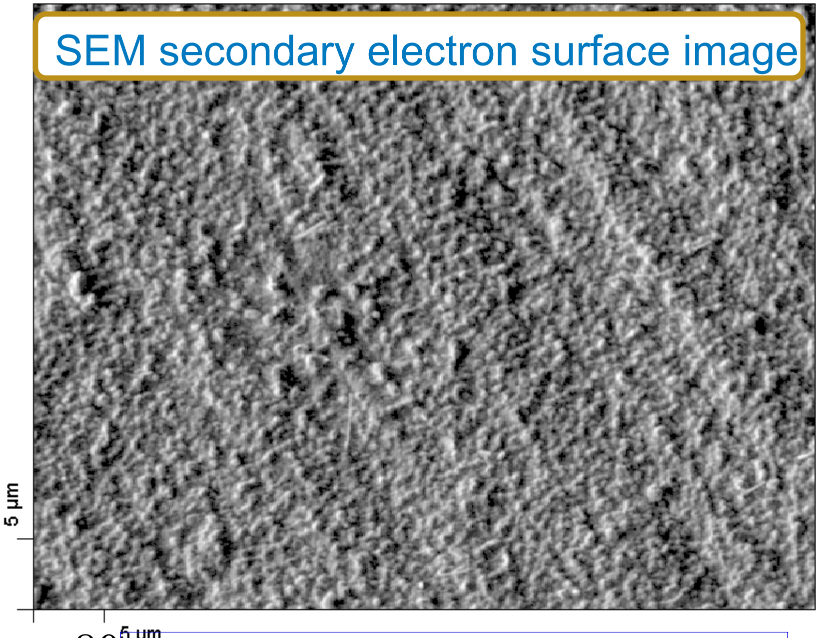
Then, Why AL29-4C ?

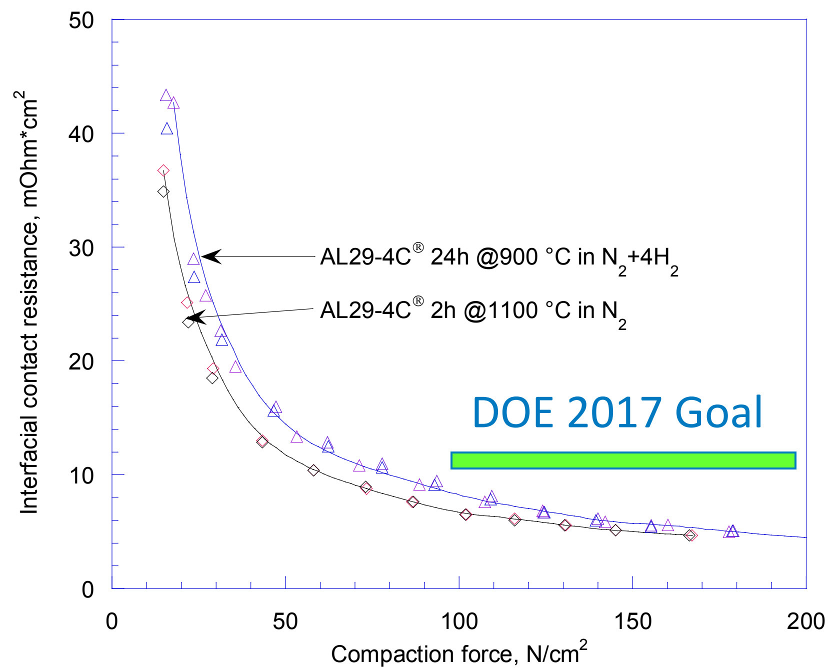
- Fe-Cr29-Mo4-Mn0.5, Similar chemical composition with AISI446;
- More Cr rich for continuous CrxN;
- Representative commercial superferritic alloy
- Lower treating temperature *ca*. 900 C;
- Industry available atmosphere, N_2-$4H_2$.

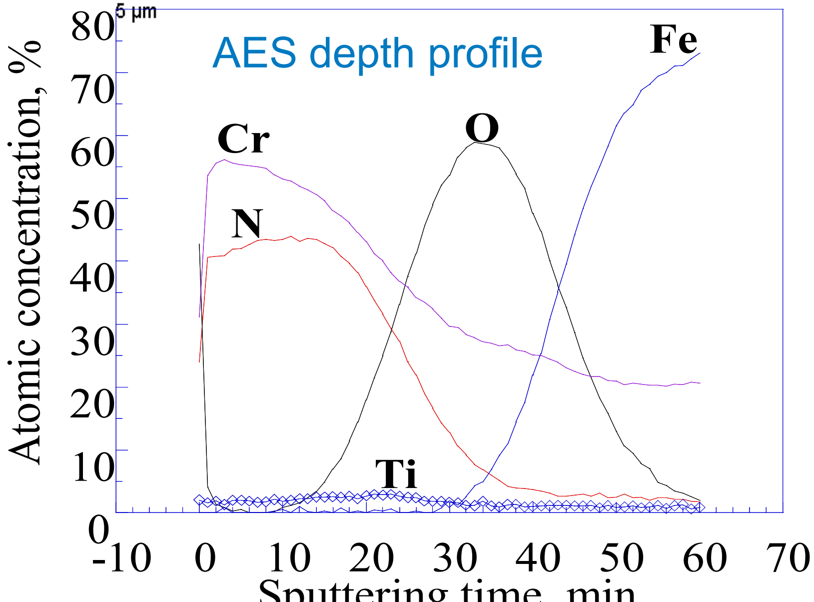


1. Similar to nitrided AISI446 in pure N_2 at 1100 C;
2. Oxygen impurity in N_2-$4H_2$ resulted in a range of surface nitridation responses;
3. Oxygen impurity is key factor. Pre-oxidation is needed to make surface nitride layer.

SEM image for AL29-4C® nitrided at 800-900 C in N_2-4H_2.





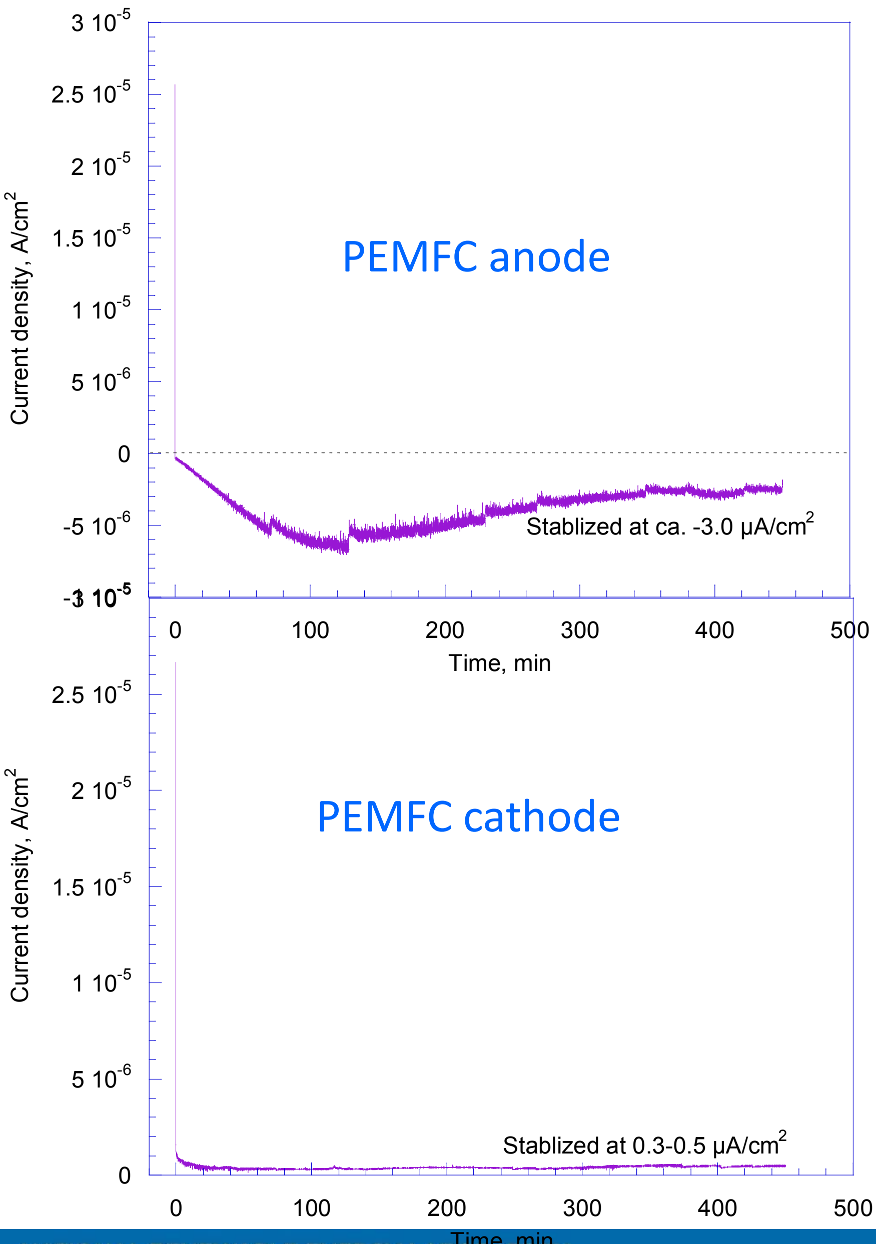


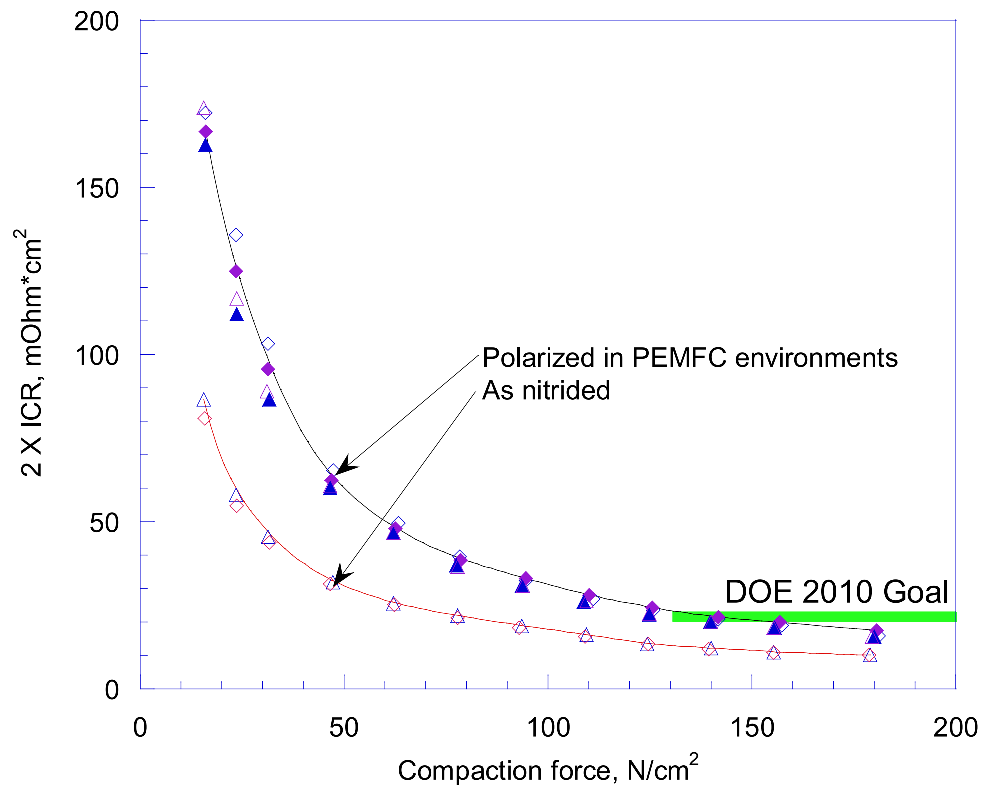
✓Longer time (17-24h) needed to have similar ICR at lower temperature;

✓Oxygen impurity factor can be improved with a pre-oxidation.

M. P. Brady, H. Wang, B. Yang, J. A. Turner, M. Bordignon, R. Molins, M. Abd Elhamid, L. Lipp, L. R. Walker: *Int. J. Hydrogen Energy*, 32 (2007) 3778.

Anodic behavior in PEMFC environments and post ICR





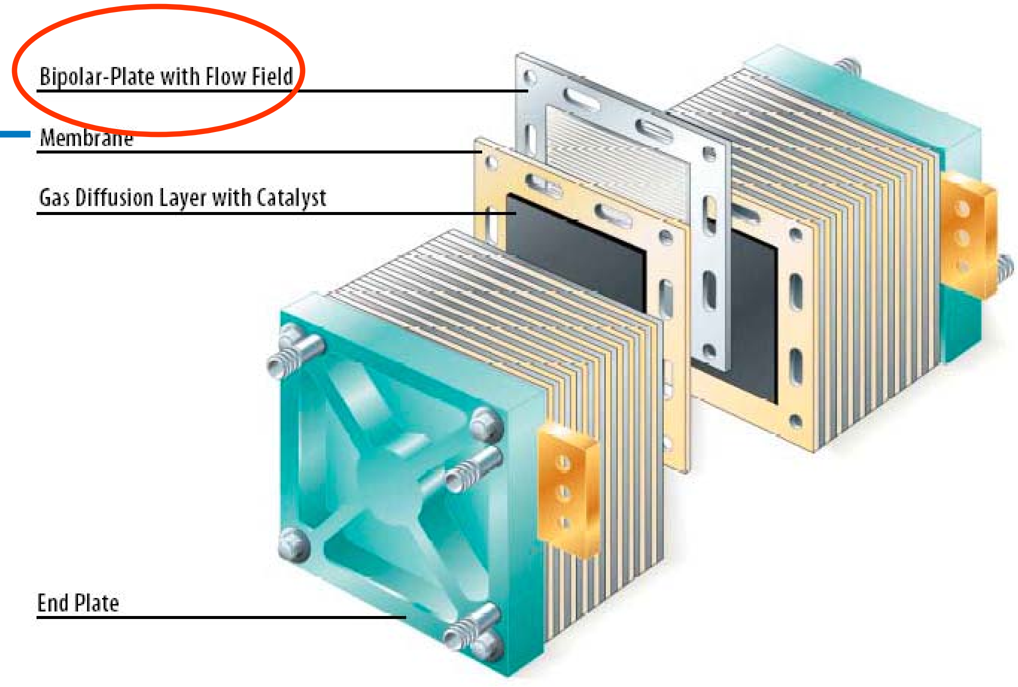
- ➢Some repeatability issues
- ➢Exclusive Cr-nitride surface can be obtained if all factors controlled correctly!

➔work moved to V alloying and quartz lamp nitriding (Dr. More's Keynote talk)

Summary Remarks (3)

- Successful development of nitrided Fe-based alloys (AISI 446 and AL29-4C).
- Nitridation of SS foils using pre-oxidation and nitriding cycle yielded mixed nitride/oxide surface layer with significantly improvement in ICR and corrosion resistance.
- Drawback was the 800-900C runs done for 24 h (long cycle = high cost). Likely solution is short preoxidation and then nitride quickly in purified N2-4H2 environment. Refer to Dr. More's talk about quartz lamp nitriding.

Outline



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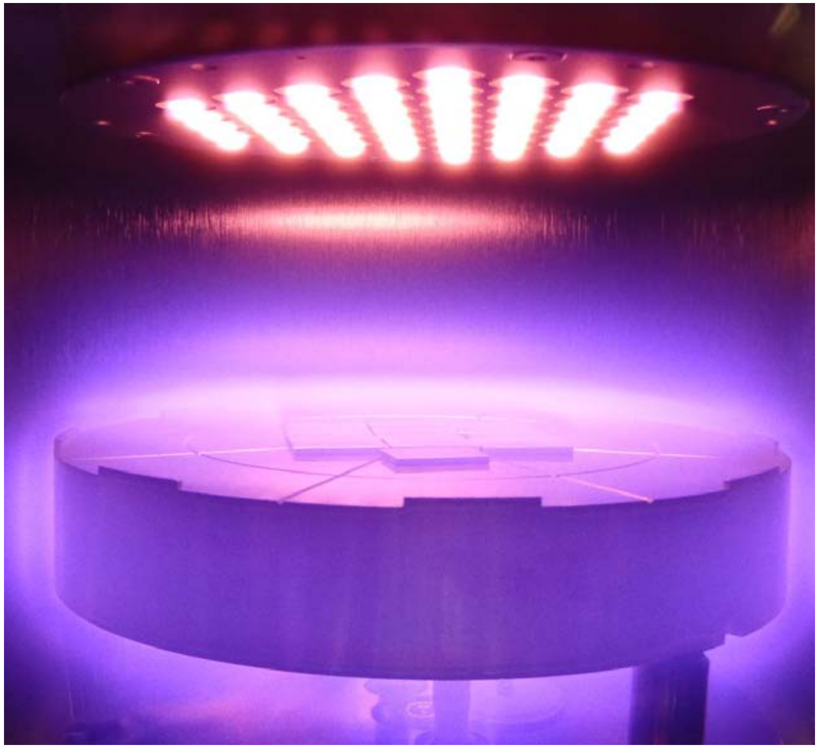
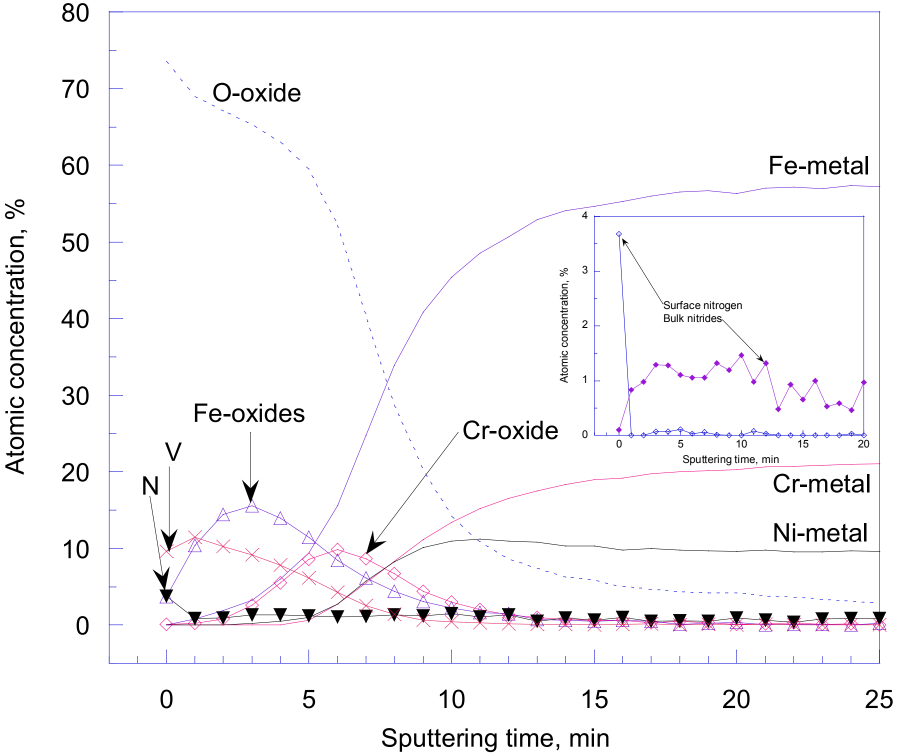
Plasma nitridation

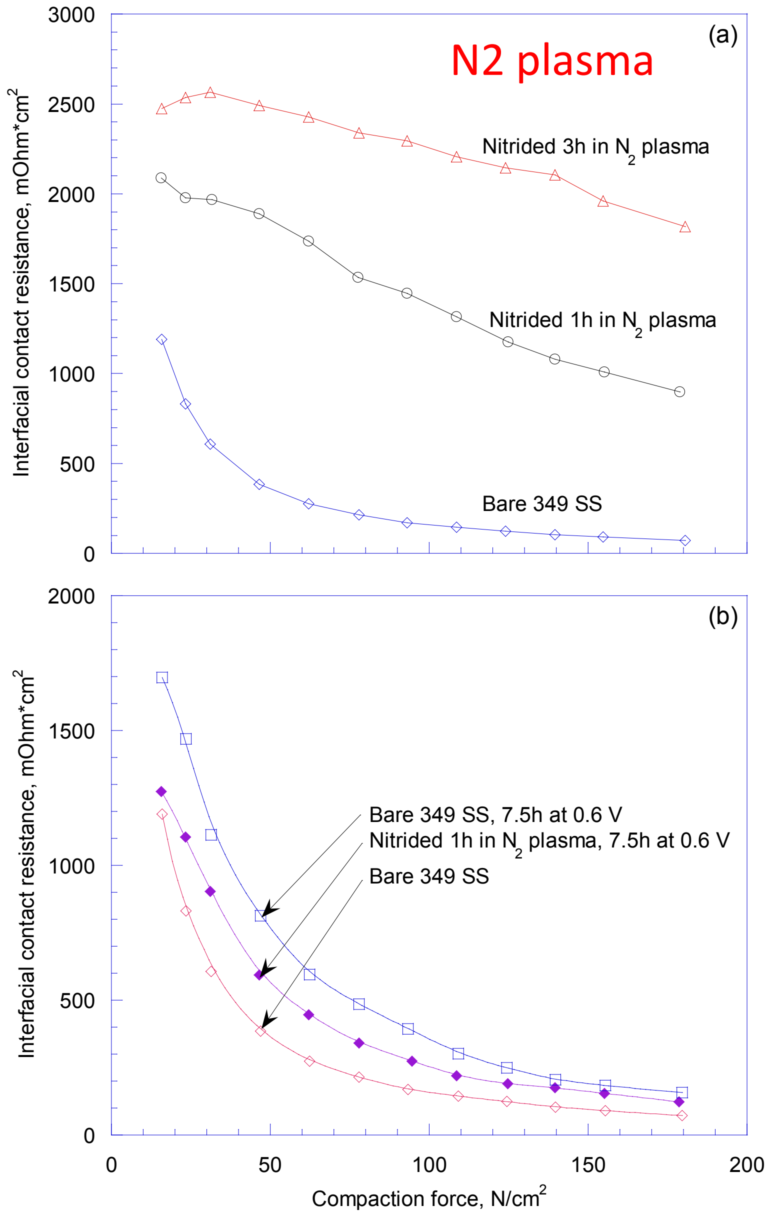
Advantage:

- Economical and conventional process
- Corrosion resistance layer
- Likely conductive
- Possible solution?



Plasma nitridation- N2 plasma treated 349



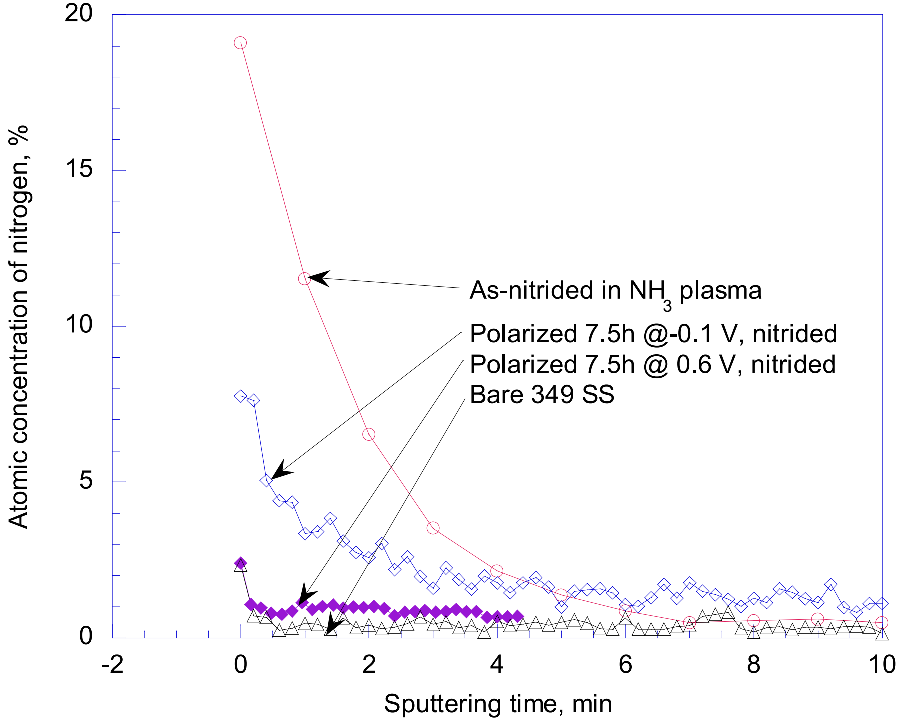


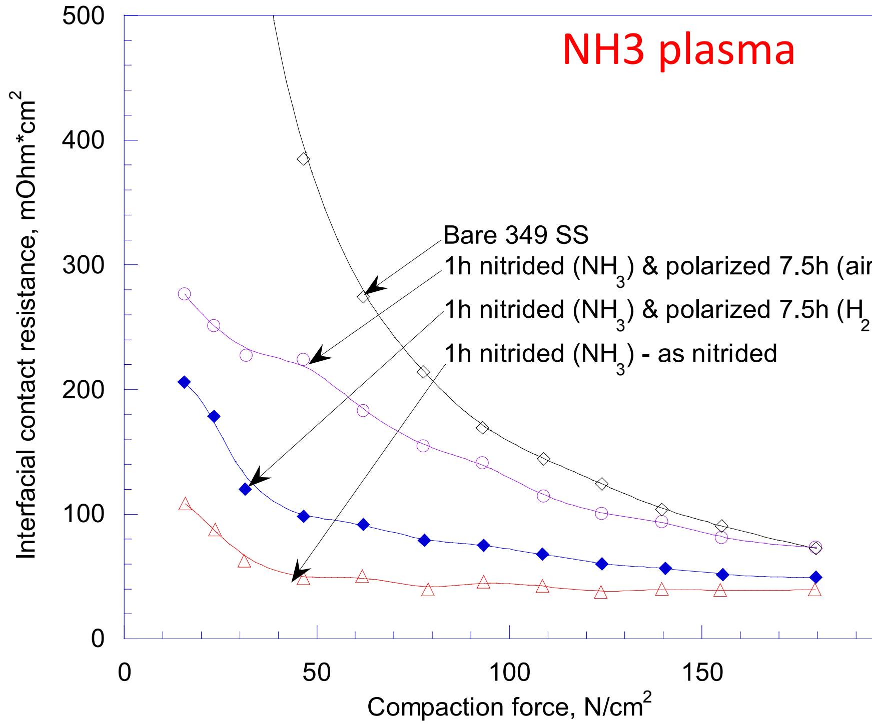
- **Similar corrosion resistance (with bare 349)**
- **ICR increase due to N2 plasma**
- **Thicker oxide film formed**

Heli Wang, Glenn Teeter, John A. Turner,
J Fuel Cell Sci. Tech. 7 (2010) 021018

Plasma nitridation- NH3 plasma treated 349

- Similar corrosion resistance (with bare 349)
- ICR decrease due to NH3 plasma
- Mixed nitride and oxide (Cr mainly) layer. Kept after polarization
- ICR related to the Cr-nitrides





New plasma equipment installed
New tests with high N-steels
Results may be reported soon….

Heli Wang, Glenn Teeter, John A. Turner, *J Fuel Cell Sci. Tech*. 7 (2010) 021019

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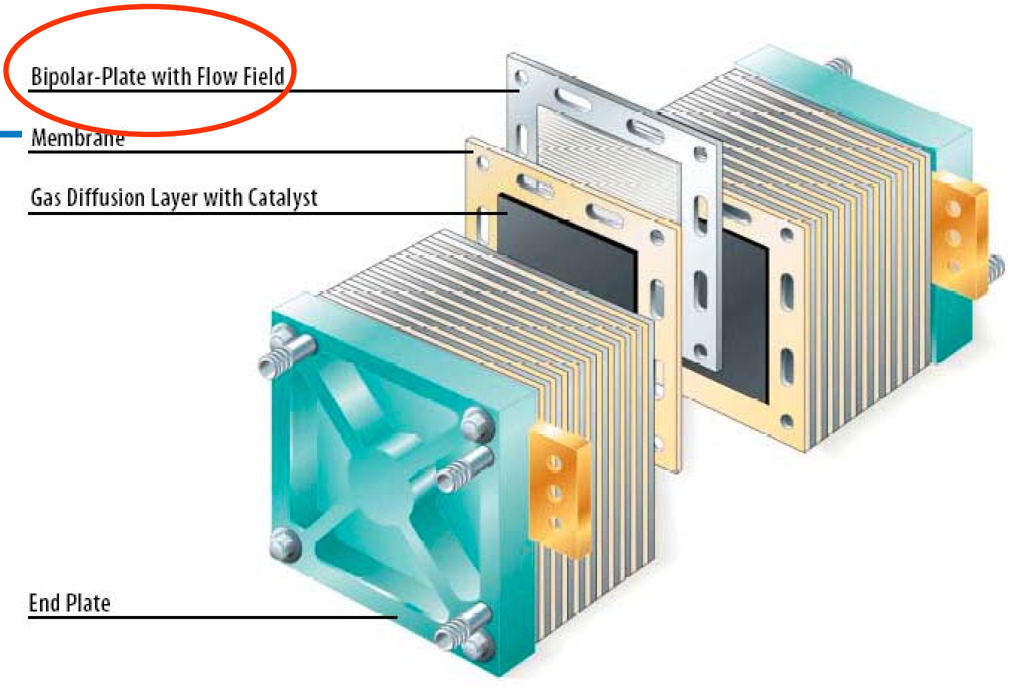

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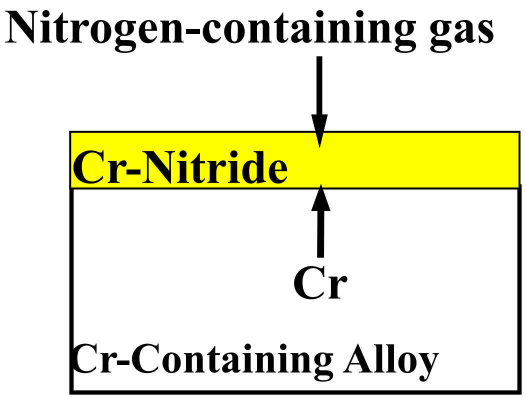
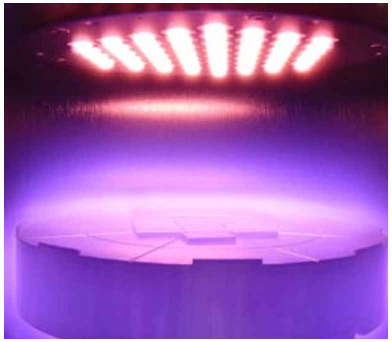
Electrochemical nitridation1

- Nitridation can be done via gas phase (thermal, atmosphere control, alloy design…)
- Nitridation can be done via plasma (plasma energy, bias, heated…)
- **Could nitridation be done via liquid phase? (possible lower temperature, lower energy use…)**
  - Yes

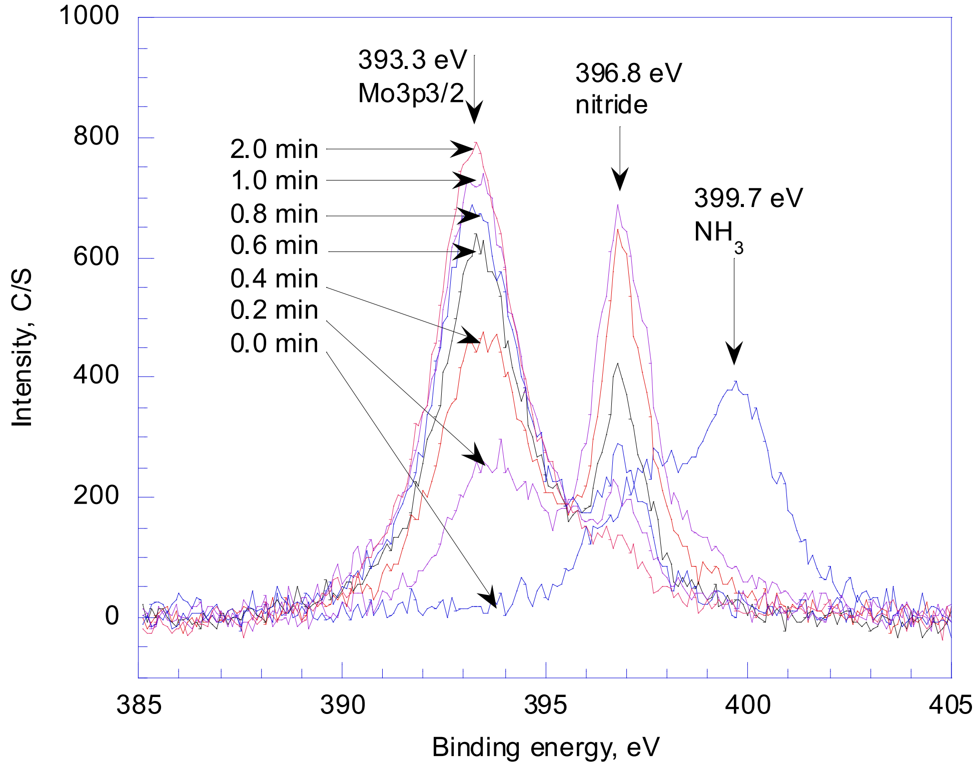


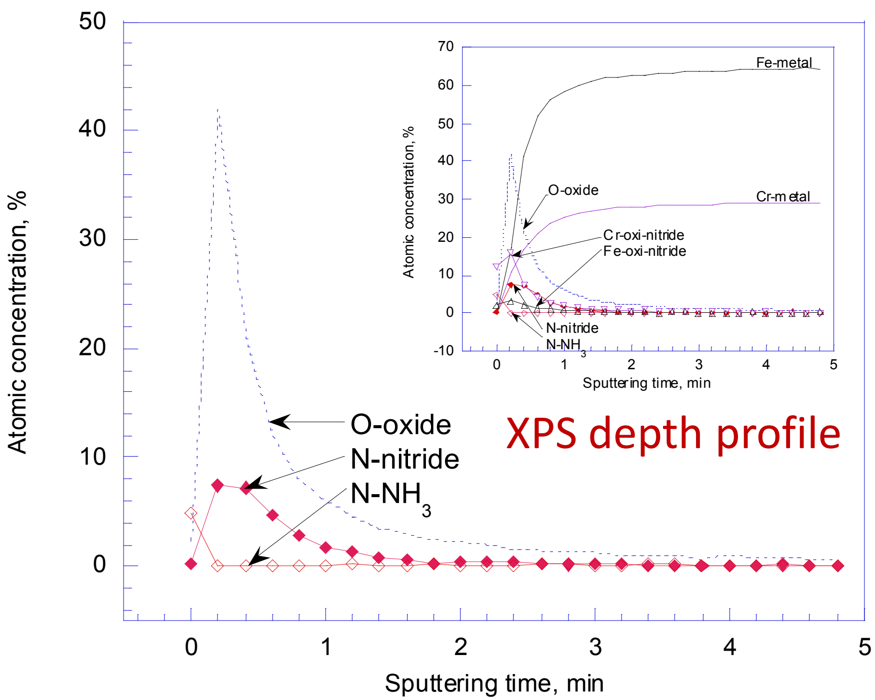


Electrochemical nitridation2

- Room temperature
- Holding for some time at cathodic applied potentials
- Nitride layer forms!

N1s X-ray photoelectron spectrum

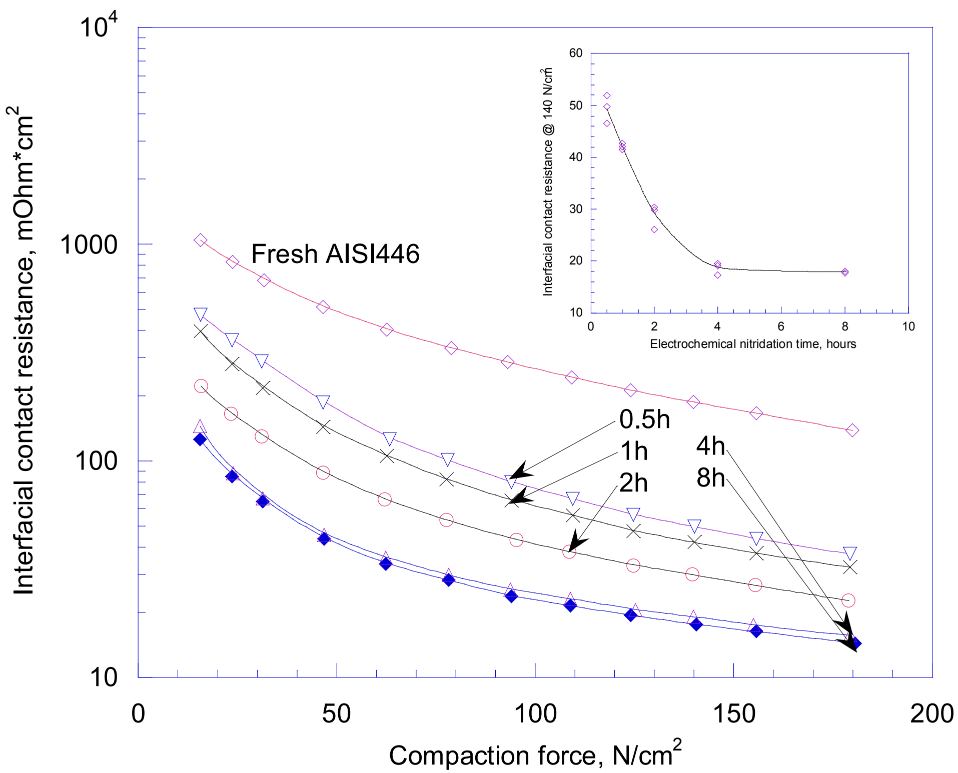


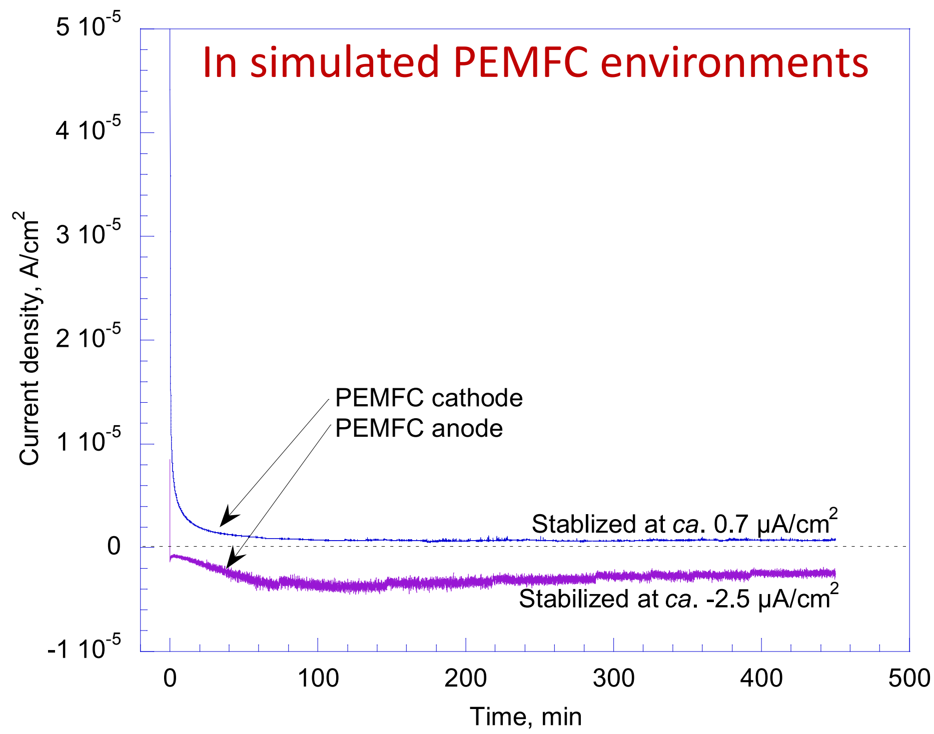


Heli Wang, Glenn Teeter and John A. Turner, *J. Mater. Chem.*, 21 (2011) 2064.

Electrochemical nitridation3

- **Excellent corrosion resistance in simulated PEMFC environments**
- **Low ICR, lower with holding period**

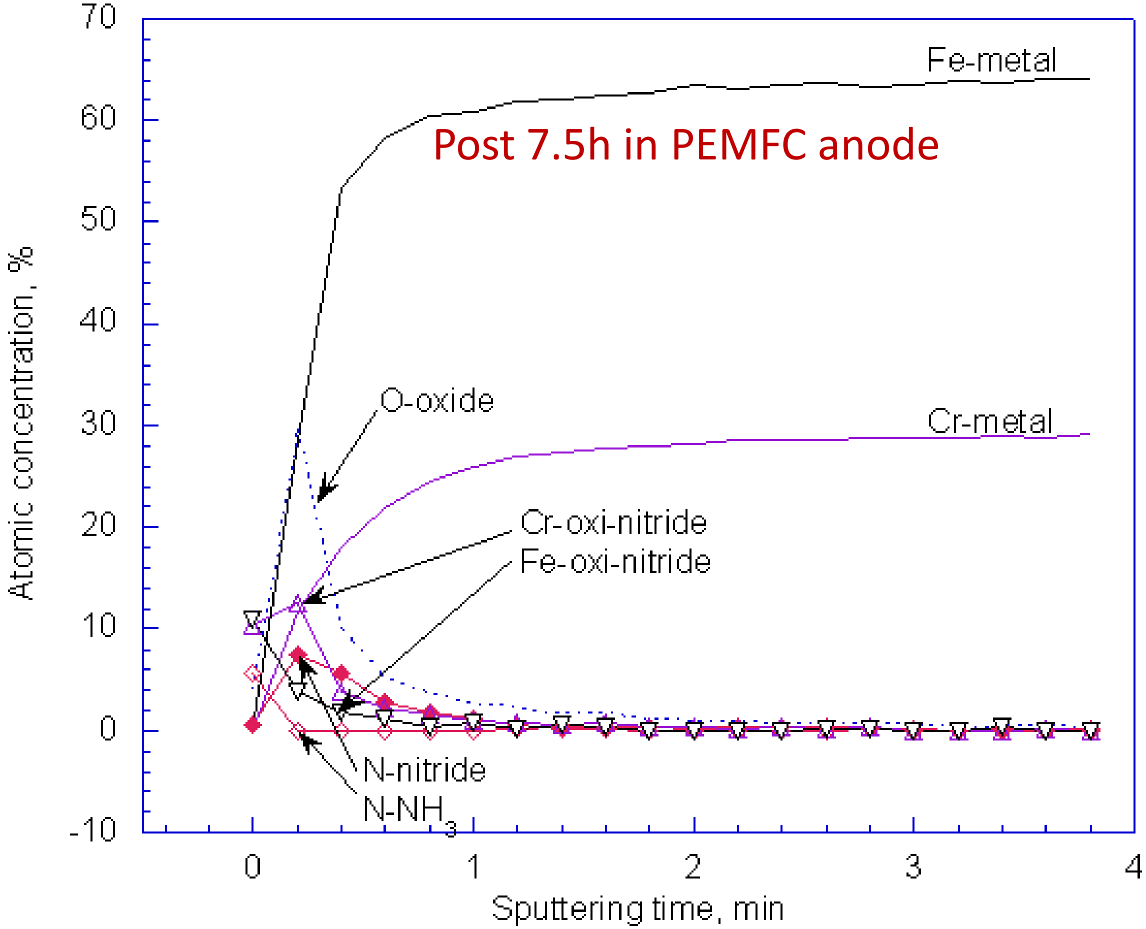




Heli Wang, John A. Turner
Int. J. Hydrogen Energy, 36 (2011) 13008.

Electrochemical nitridation4

Nitrogen-incorporated oxides (oxi-nitrides) formd
Nitride layer stable



Heli Wang, John A. Turner, *Int. J. Hydrogen Energy*, 36 (2011) 13008.

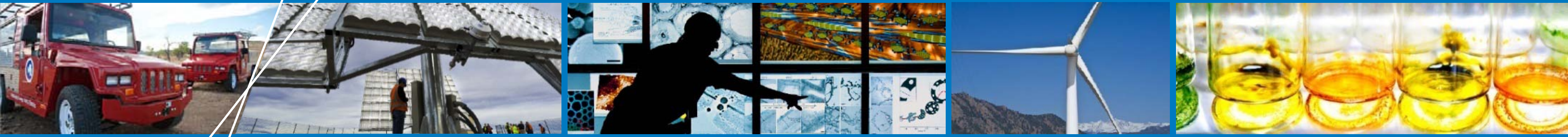
Summary Remarks (4)

- Corrosion resistant in PEMFC environments and/or ICR are issues for bare SS as bipolar plates;
- Nitrdation is one of the best solutions.
- Electrochemical nitridation provides an economic method to modify SS surface. One of the applications would be for PEMFC bipolar plates.

Acknowledgements

U.S. Department of Energy
Energy Efficiency and Renewable Energy
Fuel Cell Technologies Program

- Dr. Anders Ødegård, SINTEF
- Your attention!!



Sample Section Divider

Beneficial effect of SnO_2:F coating on the corrosion resistance of stainless steels in PEMFC environments (Original coated)

Metallic ions after 7.5h in PEMFC environments, average 3 samples

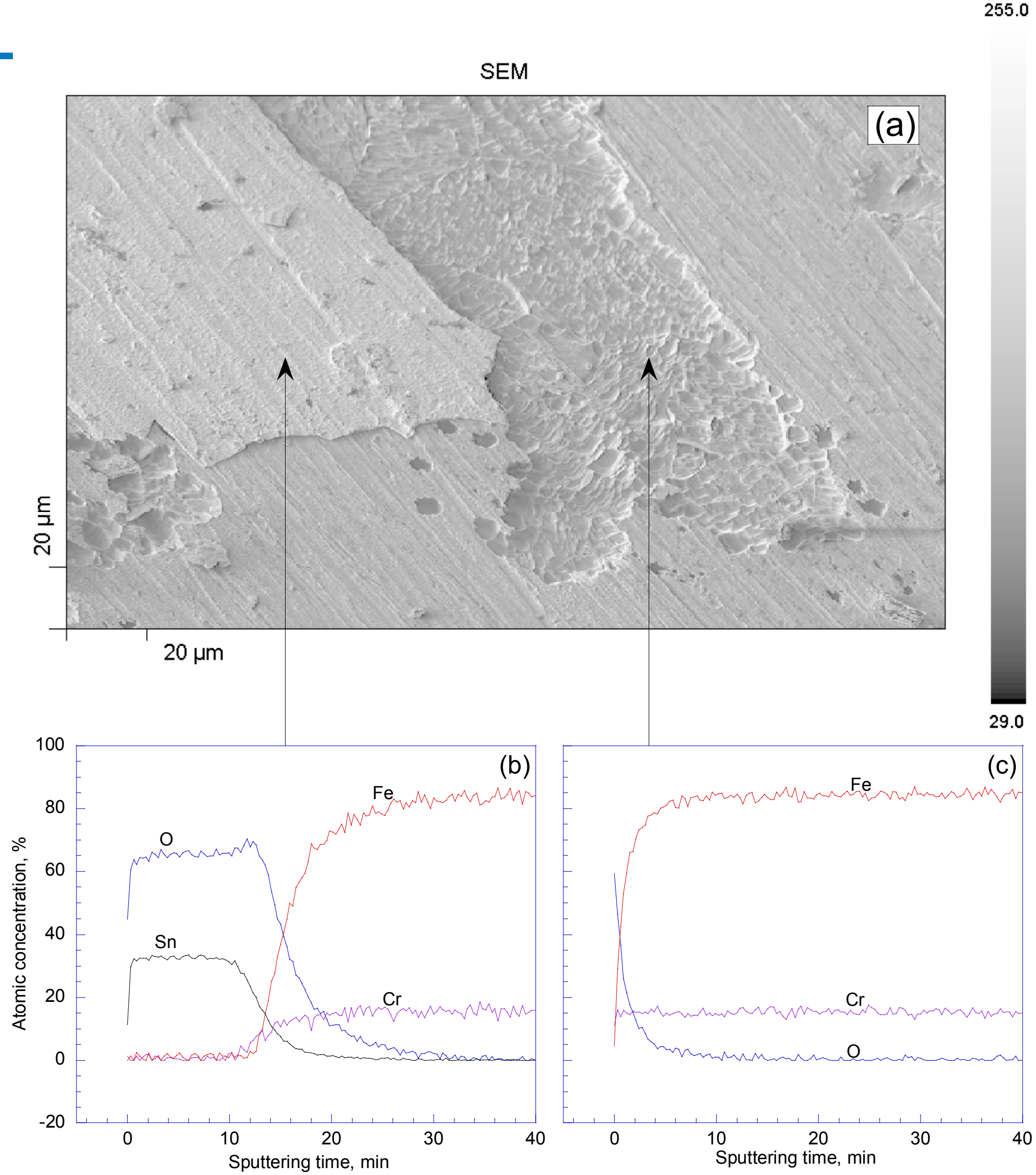
Material	Ion concentration in PEMFC anode environment after 7.5h, ppm				Ion concentration in PEMFC cathode environment after 7.5h, ppm			
	Fe	Cr	Ni	Sn	Fe	Cr	Ni	Sn
316L	21.18	4.60	2.49		9.02	1.94	1.41	
317L	3.98	0.65	0.39		1.29	-	-	
349™	1.70	0.12	-		1.47			
2205	1.8	-	-		2.3	-	-	
SnO_2:F/316L	10.83	1.97	1.38	0.49	1.12	0.10	0.11	-
SnO_2:F/317L	4.03	0.69	0.56	0.19	0.87	-	-	-
SnO_2:F/349™	1.27	-	-	0.10	1.07	-	-	-
SnO_2:F/2205	3.7	-	-		1.9	-	-	

Material	Ion content after 7.5h in PEMFC anode (H_2) environment, ppm				Ion content after 7.5h in PEMFC cathode (air) environment, ppm			
	Fe	Cr	Ni	Sn	Fe	Cr	Ni	Sn
AISI441	622.9	135.7	1.07		462.8	101.2	0.95	
AISI444	141.5	37.86	0.30		328.3	67.97	0.94	
AISI446	1.46	-	-		0.99	-	-	
SnO_2:F/AISI441	24.15	4.51	-	2.42	330.3	73.53	0.60	22.76
SnO_2:F/AISI444	12.70	2.09	-	1.76	64.42	13.73	0.22	4.50
SnO_2:F/AISI446	1.24	-	-	-	0.98	-	-	-

Heli Wang et al., *J. Power Sources* **171** (2007) 567.; **170** (2007) 387.; **178** (2008) 238.

Post surface investigation

Coating gone!
Heavy corrosion for un-covered area!

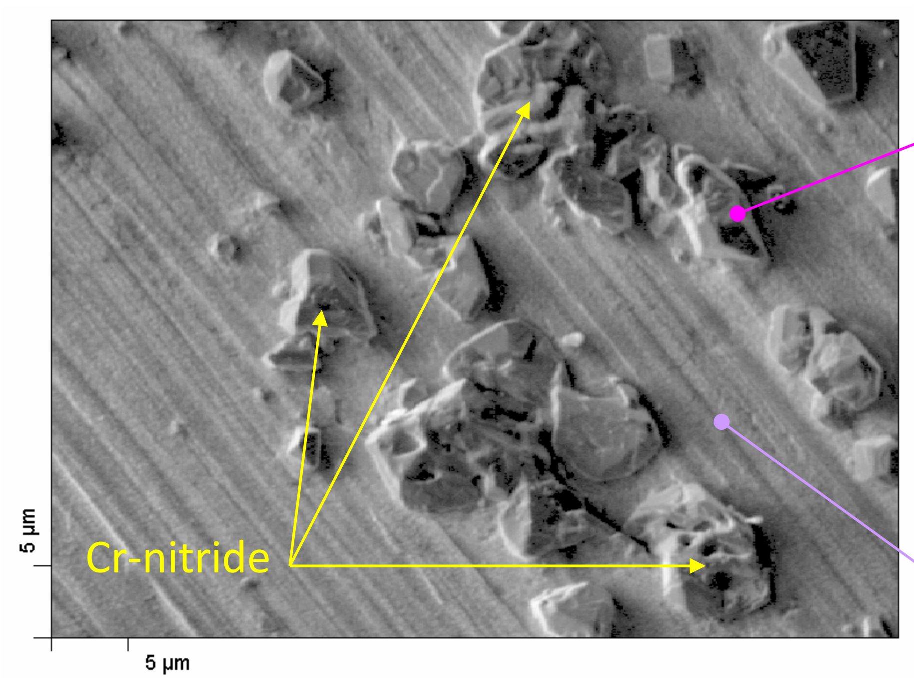


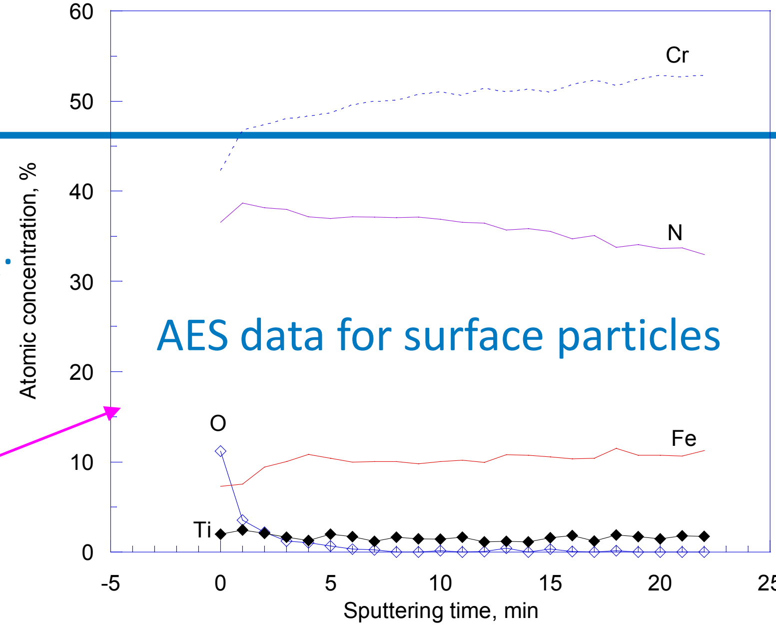
(a) SEM image for modified coated AISI444 steel after 7.5h in PEMFC anode environment; (b) AES depth profile for covered area; (c) AES depth profile for un-covered area.

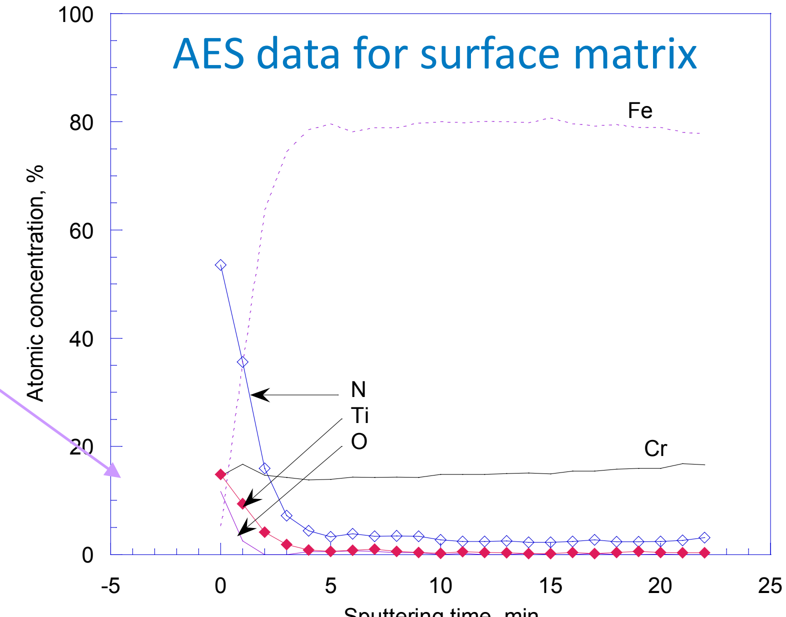
Heli Wang, John A. Turner, Xiaonan Li, Glenn Teeter, *J. Power Sources* **178** (2008) 238.

SEM image & AES analysis for AL29-4C® nitrided 2h @ 1100 C in N_2-$4H_2$.

SEM secondary electron surface image for AL29-4C after 2h nitrided at 1100 C in flowing, purified N_2-$4H_2$.





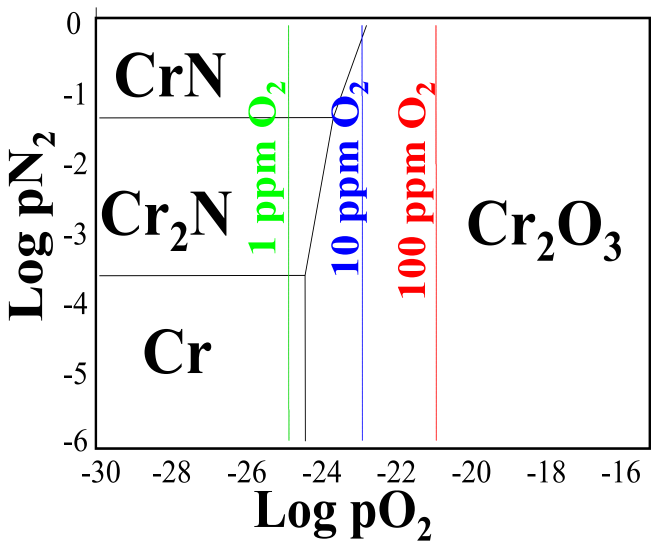


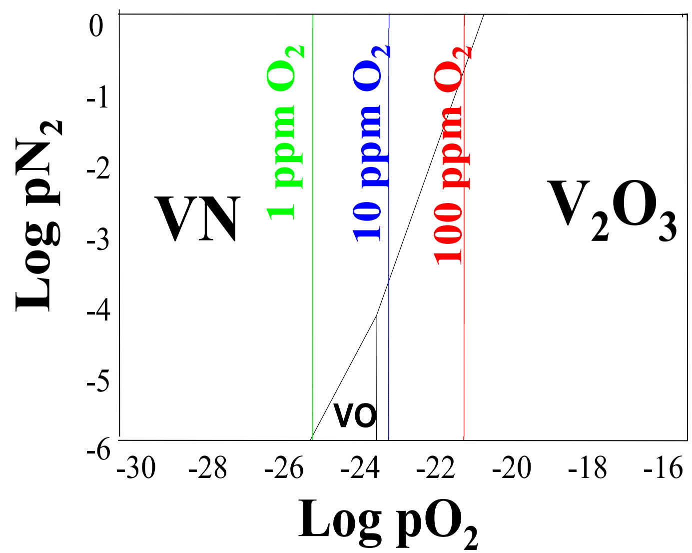
The estimated sputtering rate was ~50 nm/minute.

M. P. Brady, H. Wang, B. Yang, J. A. Turner, M. Bordignon, R. Molins, M. Abd Elhamid, L. Lipp, L. R. Walker: *Int. J. Hydrogen Energy*, 32 (2007) 3778.

V Additions Destabilize Oxide Relative to Nitride Compared to Cr

900 C Predominance Diagrams

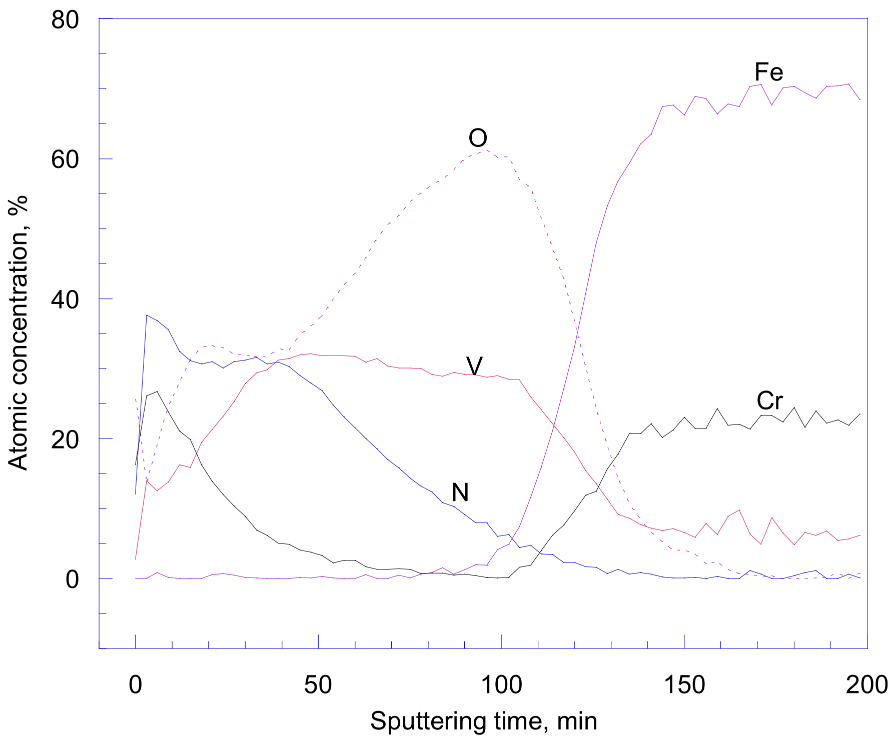




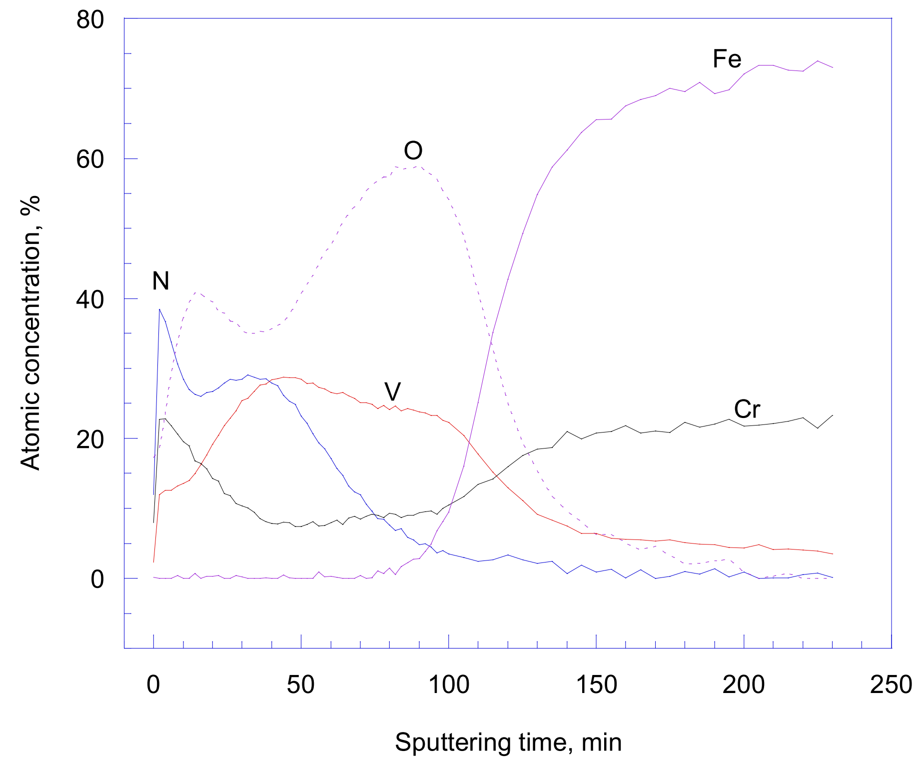
- Order of magnitude greater O_2 impurity stability for VN relative to CrN at 900 C in N_2-$4H_2$ (100 vs 10 ppm O_2)
- V works because Cr_2O_3-V_2O_3; Cr_2N-V_2N; CrN-VN all mutually soluble
- V_2O_3 and Cr-doped V_2O_3 also conductive-combined with intermixed morphology and N_2-doping yields good ICR values

B. Yang, M. P. Brady, H. Wang, J. A. Turner, K. L. More, D. J. Young, P. F. Tortorelli, E. A. Payzant and L. R. Walker: *Journal of Power Sources* 174, 228(2007).

Auger Electron Spectroscopy (AES) of Nitrded Fe-27Cr-6V



As Nitrded



After 7.5h in PEMFC cathode environment

- 7.5h Polarization showed very little effect on the surface chemistry! (similar results under H_2-purged anodic conditions)
- No Fe detected in nitrided surface, **oxygen present** in surface

B. Yang, M. P. Brady, H. Wang, J. A. Turner, K. L. More, D. J. Young, P. F. Tortorelli, E. A. Payzant and L. R. Walker: *Journal of Power Sources* 174, 228(2007).