Membrane Durability in PEM Fuel Cells

Chemical Degradation

Vishal Mittal and Sathya Motupally
UTC Power
South Windsor, CT 06074

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Outline

Membrane Durability

Chemical degradation mechanism

Impact of HT and low RH

Impact of cell components

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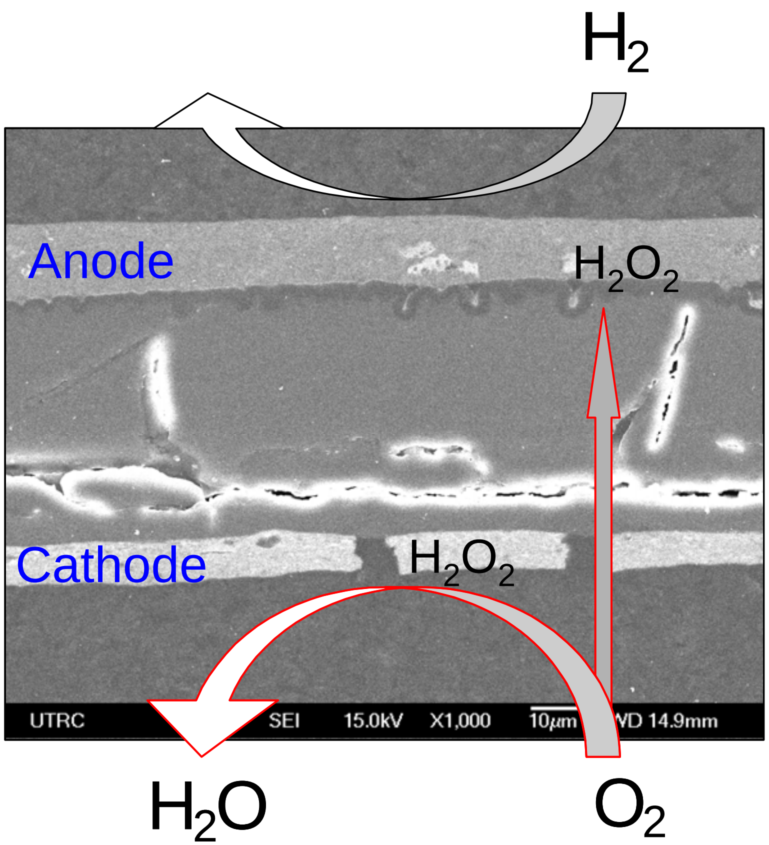
Overview of mechanism



H_2O_2 formation → *Radical formation* → *Attack of polymer weak sites*

→ *Material properties degrade* → *Localized stress promotes cracks, fissures* → *Crossover failure occurs*

$$H_2 + O_2\ (\ldots) \rightarrow OH\bullet\ (\&\ OOH\bullet\ ) + \text{polymer-}CF_3 \rightarrow F^-$$

Measured in reactant effluent (FER)

D. E. Curtin, R.D. Losenberg, T.J. Henry, P.C. Tangeman, M.E. Tisack *J. Power Sources* **131** 41-48 (2004).

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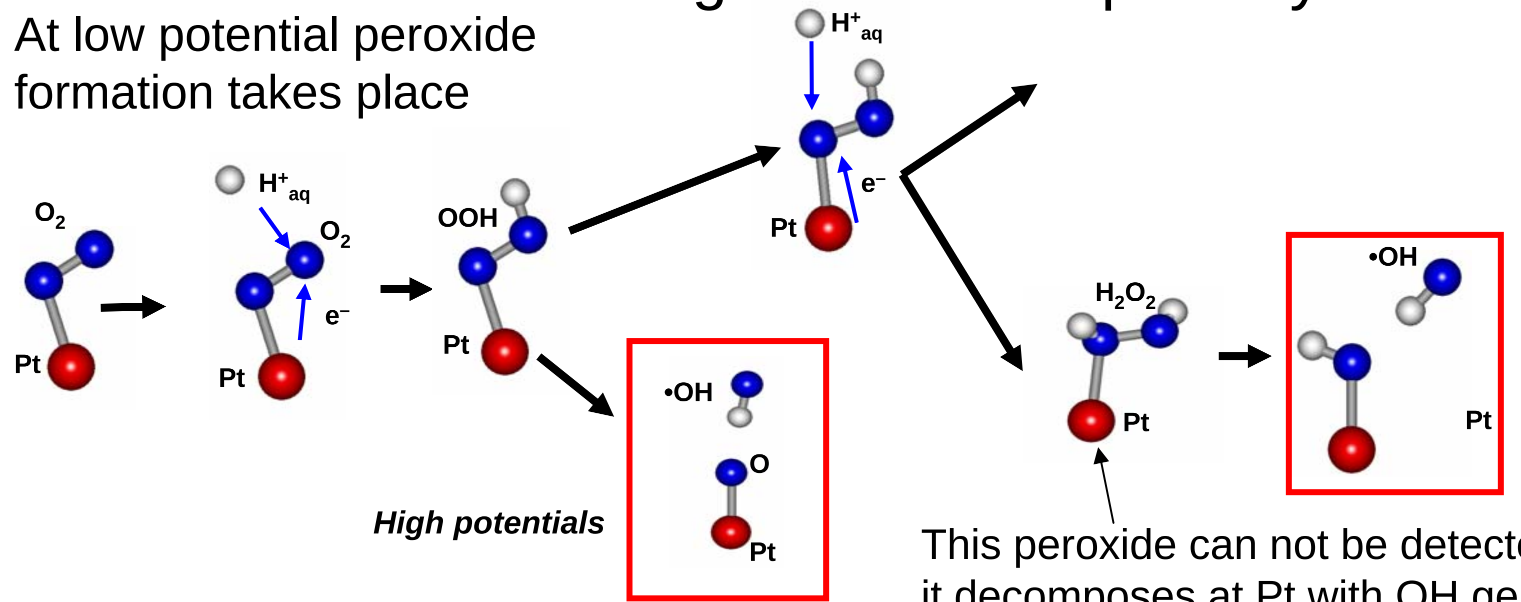
Direct mechanism of OH generation on partially covered Pt

At low potential peroxide formation takes place



This peroxide can not be detected because it decomposes at Pt with OH generation

Ea=0.0*eV* (@0V), *Ea*=0.36*eV* (@1V)

$$O_2 \rightarrow O_{2ads} + e^- + H^+ \rightarrow OOH_{ads}$$

Ea=0.54*eV*

$$OOH_{ads} \rightarrow O_{ads} + {}^{\bullet}OH$$

$$OOH_{ads} + e^- + H^+ \rightarrow H_2O_2$$

Ea=0.0*eV* (@0V), *Ea*=0.47*eV* (@1V)

$$H_2O_{2ads} \rightarrow OH_{ads} + {}^{\bullet}OH$$

Ea=0.0*eV*

Peroxide and *OH radical formation take place by ORR if oxygen molecule bonds with one Pt site*

Adsorbed peroxide decomposes with formation OH radicals at any potential if peroxide molecule bonds with one Pt site.

S. Burlatsky et al., Gordon Conference, July 2006, Bryant University, RI, USA
S. Motupally, Crete Degradation Workshop September 2007, Crete, Greece.

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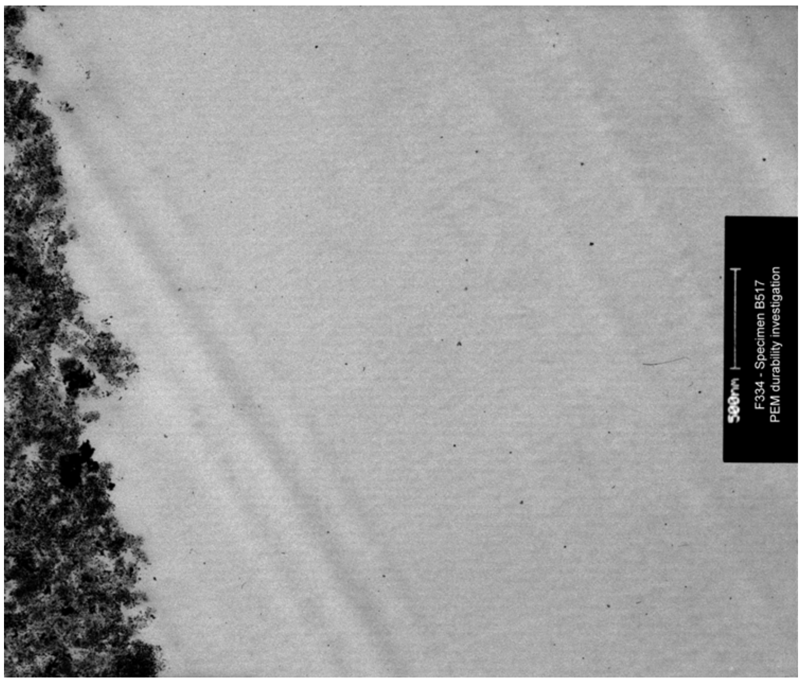
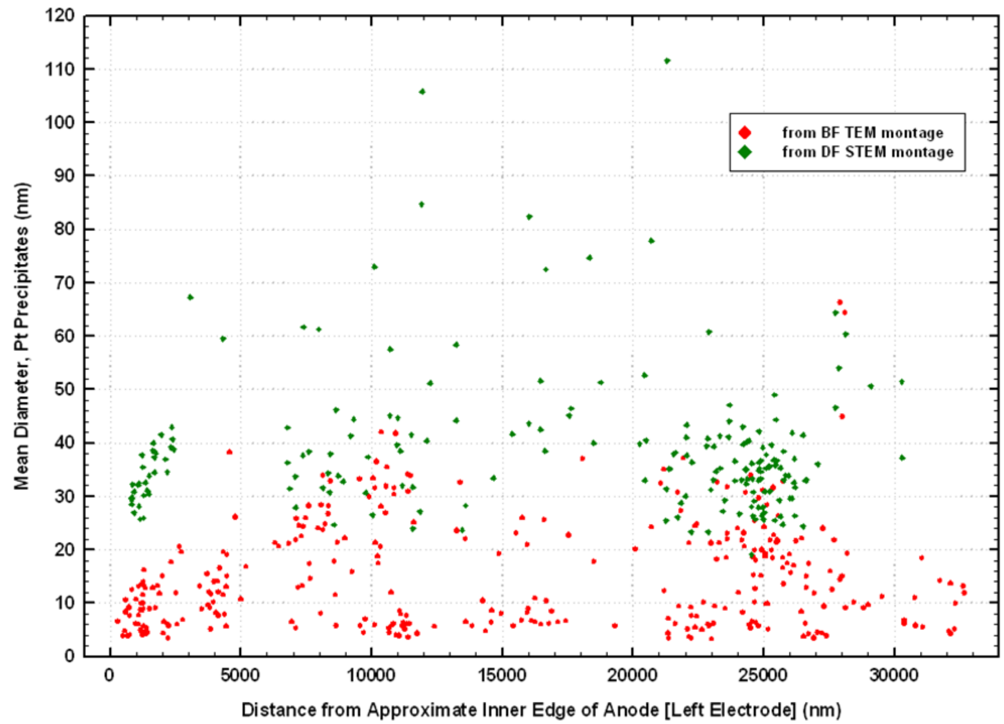
TEM analysis of degraded MEA

After OCV, 90 C, 30 % RH, ~100 hrs





~ 5 nm particles at ~300 nm spacing observed in BF TEM

S. Motupally, Crete Degradation Workshop September 2007, Crete, Greece.

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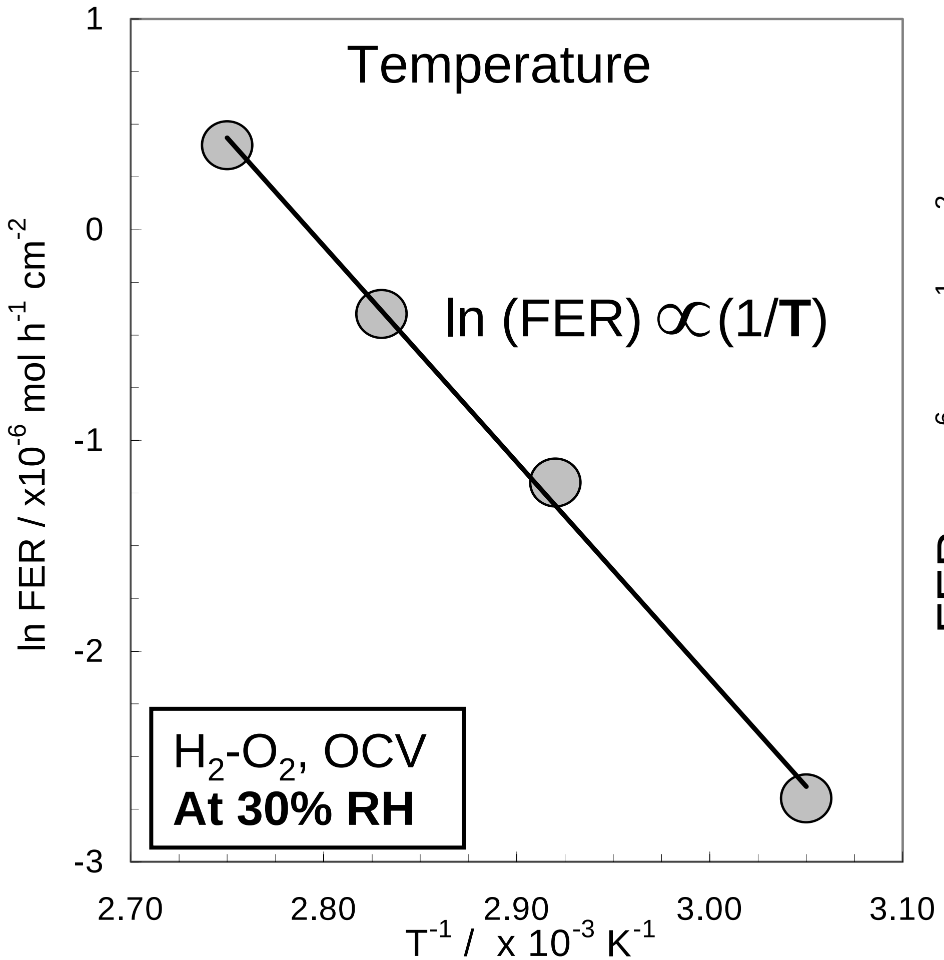
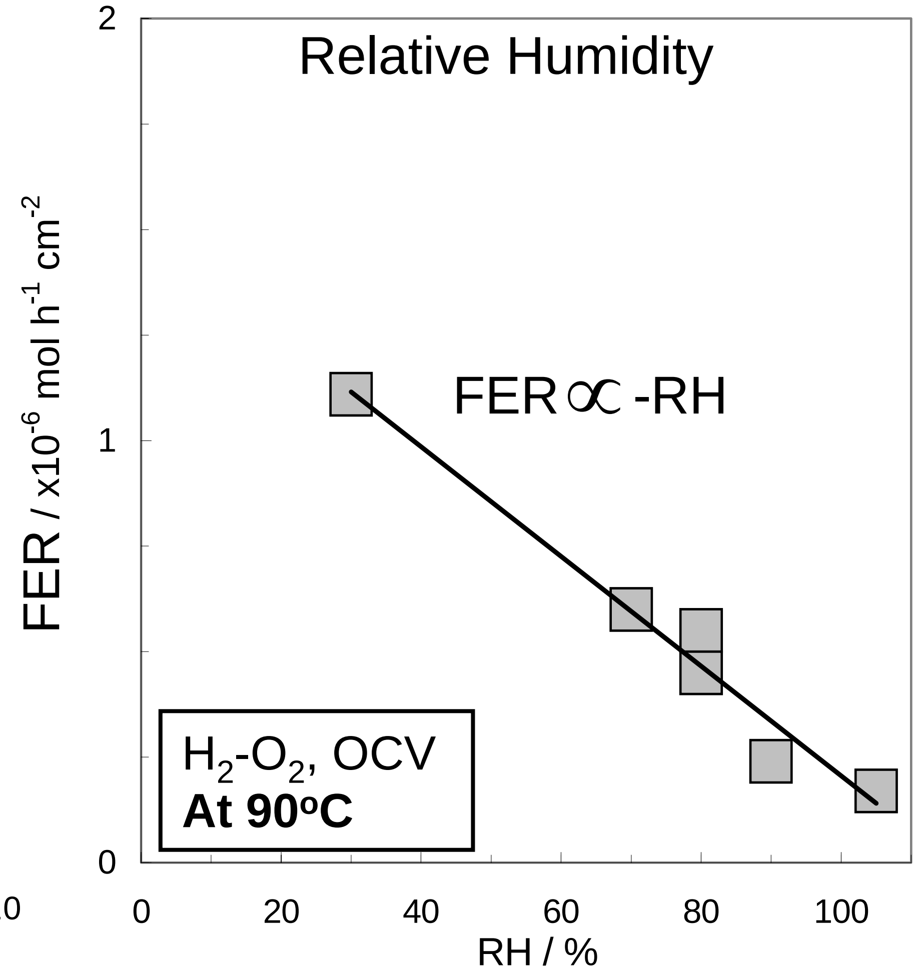
Effect of operating conditions





"FER" = Total FER = Anode FER + Cathode FER

Paik *et al.* 207th ECS Meeting, Abstract # 771, Quebec City, May 15 (2005)

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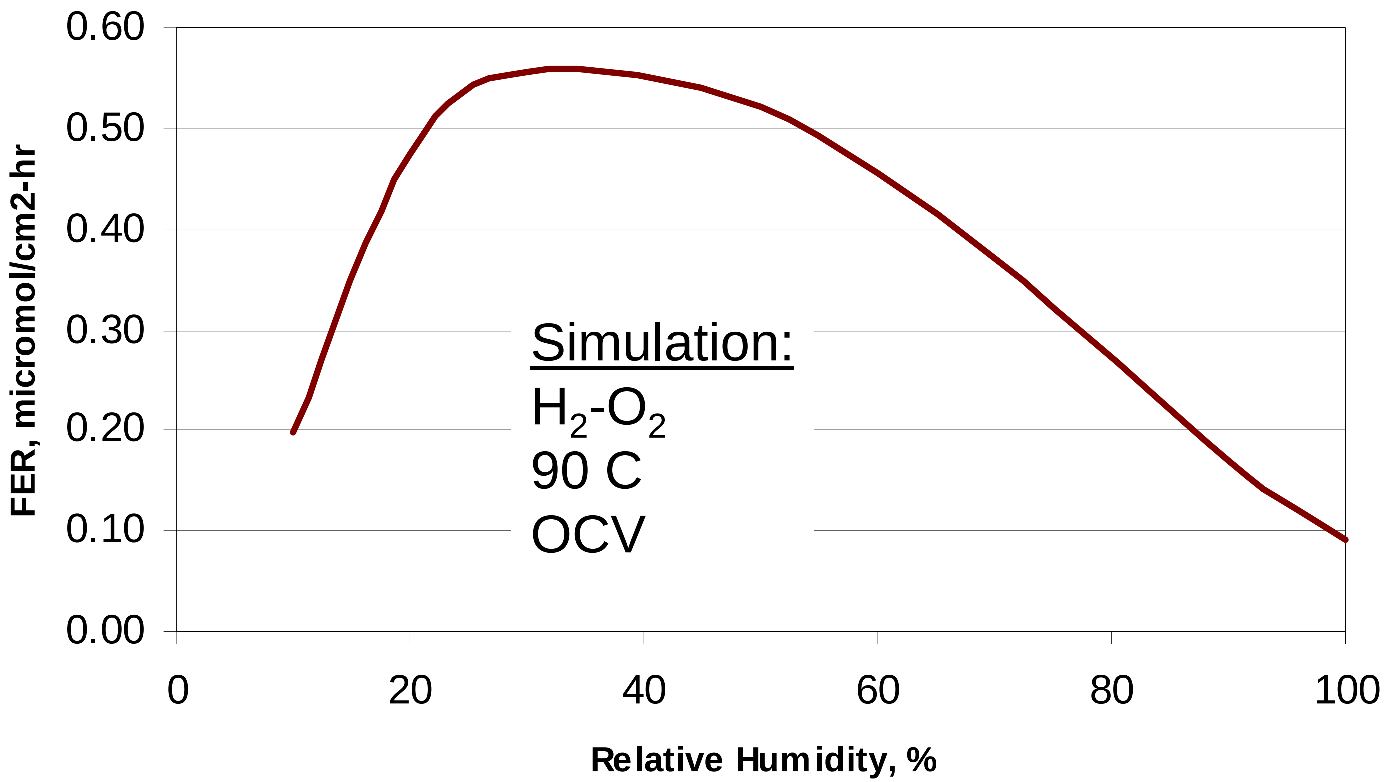
Model simulations at low RH



Lower gas cross-over
Higher gas mole fraction

High gas cross-over
Lower gas mole fraction in flow-field

S. Burlatsky et al., Gordon Conference, July 2006, Bryant University, RI, USA a

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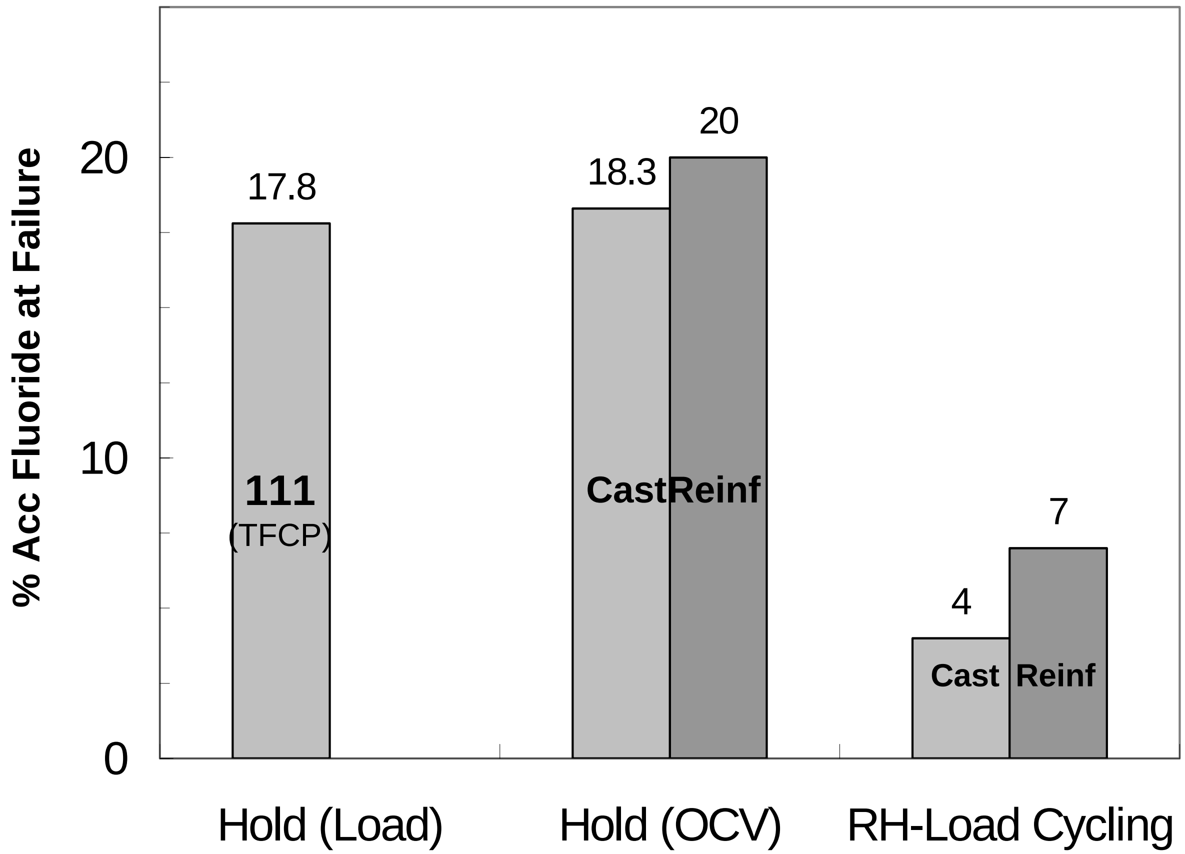
Effect of load

Hold allows more %F loss (less localized); Reinforced allows more %F loss

1. Reinforced membrane tolerates higher %Acc F loss.

2. **Hold** allows higher cumulative F loss at failure than **Cycling**.



C. Paik *et al.* 207th ECS Meeting, Abstract # 771, Quebec City, May 15 (2005)

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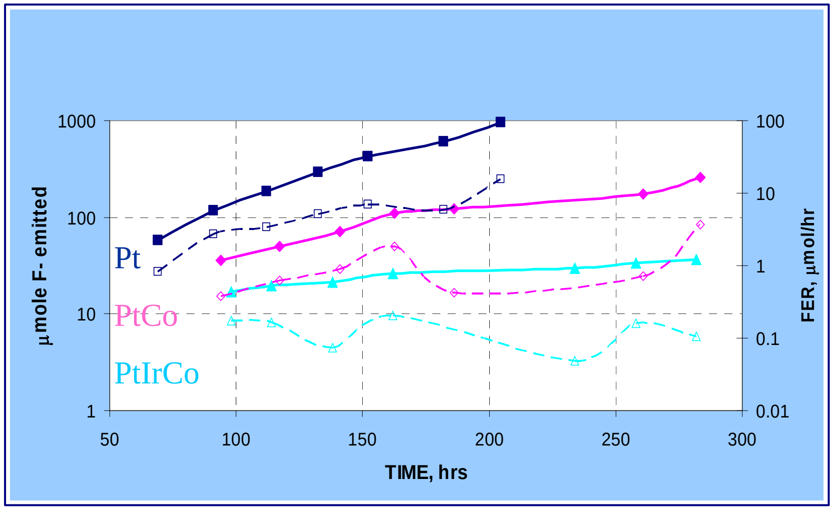
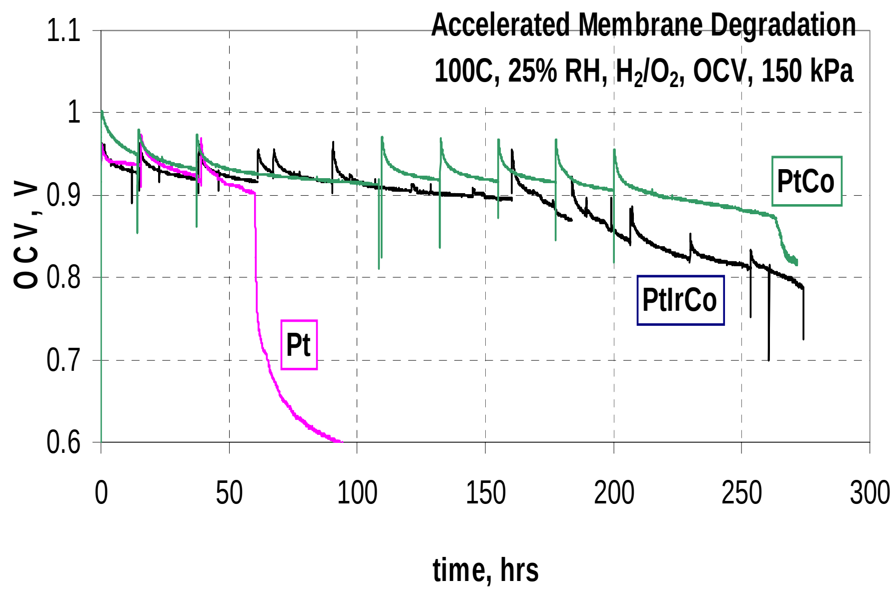
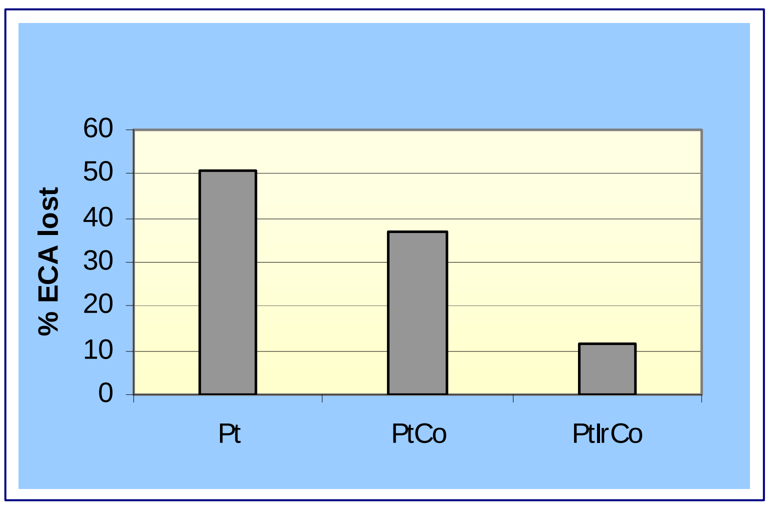
Impact of catalyst stability







FER : Pt > PtCo > PtIrCo
Membrane durability
Consistent with Pt stability

L. Protsailo, "Advances in Materials for Proton Exchange Membrane Fuel cell Systems", Asilomar Conference Grounds, Pacific Grove, CA 2005

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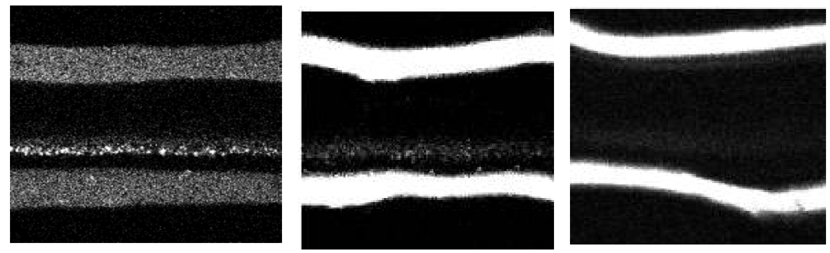
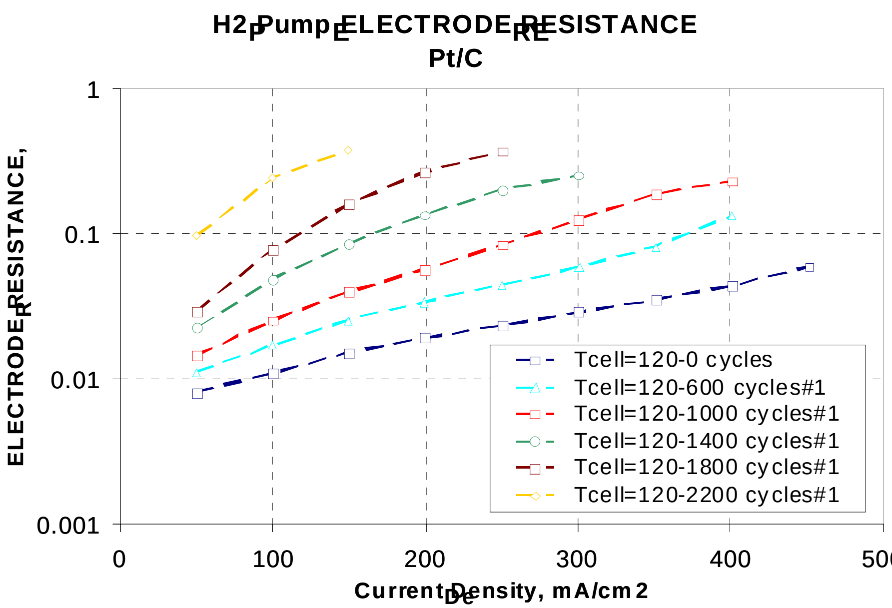
Impact on ionomer durability

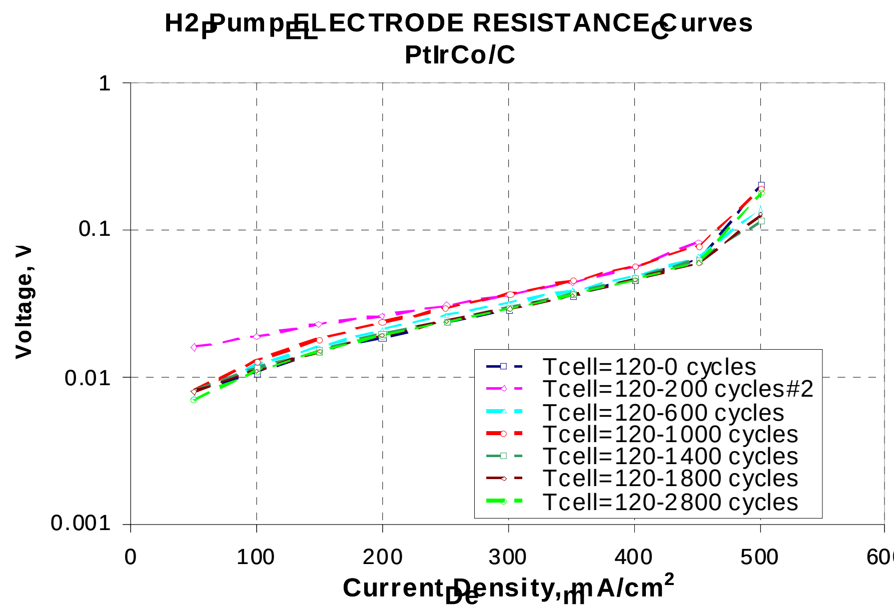
– 10 % H_2 in N_2, low utilization
– Electrode Ionic resistance changes with time
– PtIrCo cathode prevents ionomer poisoning

Pt EMPA map after cycling



Pt PtCo PtIrCo





L. Protsailo, FC20, 2006 DOE Hydrogen Program Review, May 13-16, 2006, Arlington, VA

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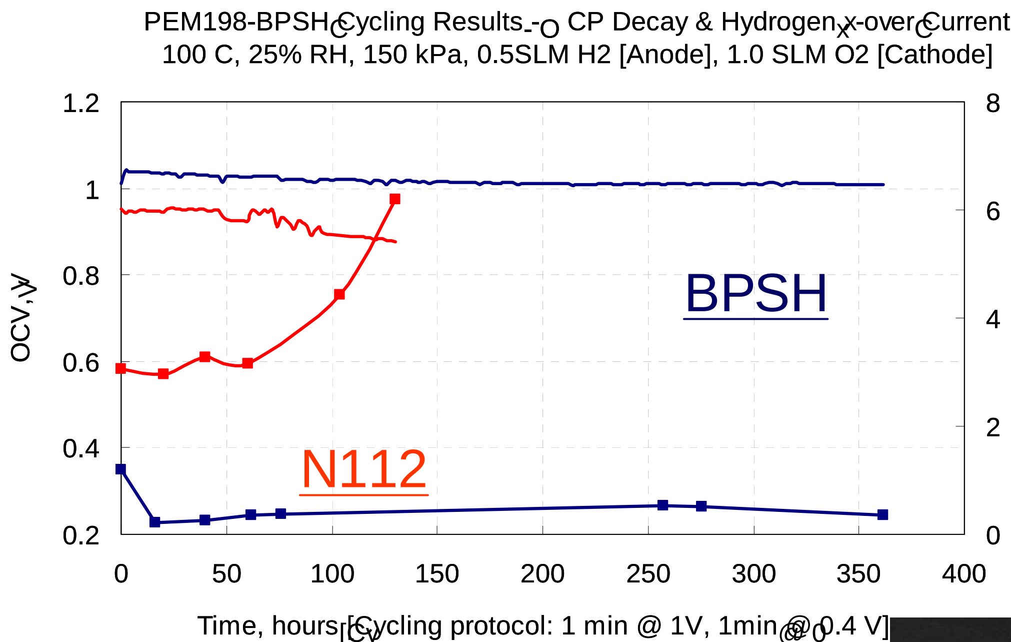
Hydrocarbon membranes

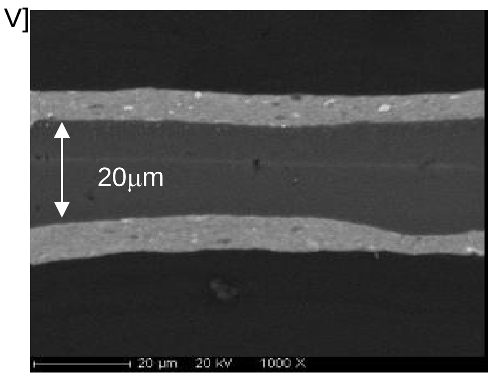


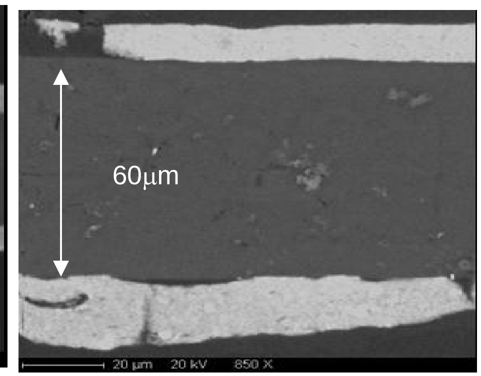
Load cycle protocol:

- 100°C, 25%RH
- 0.5 SLPM H_2/1.0 SLPM O_2
- 1min @ 1V, 1min @ 0.4V

EMPA post test analysis:

- BPSH retained its thickness in load cycle test





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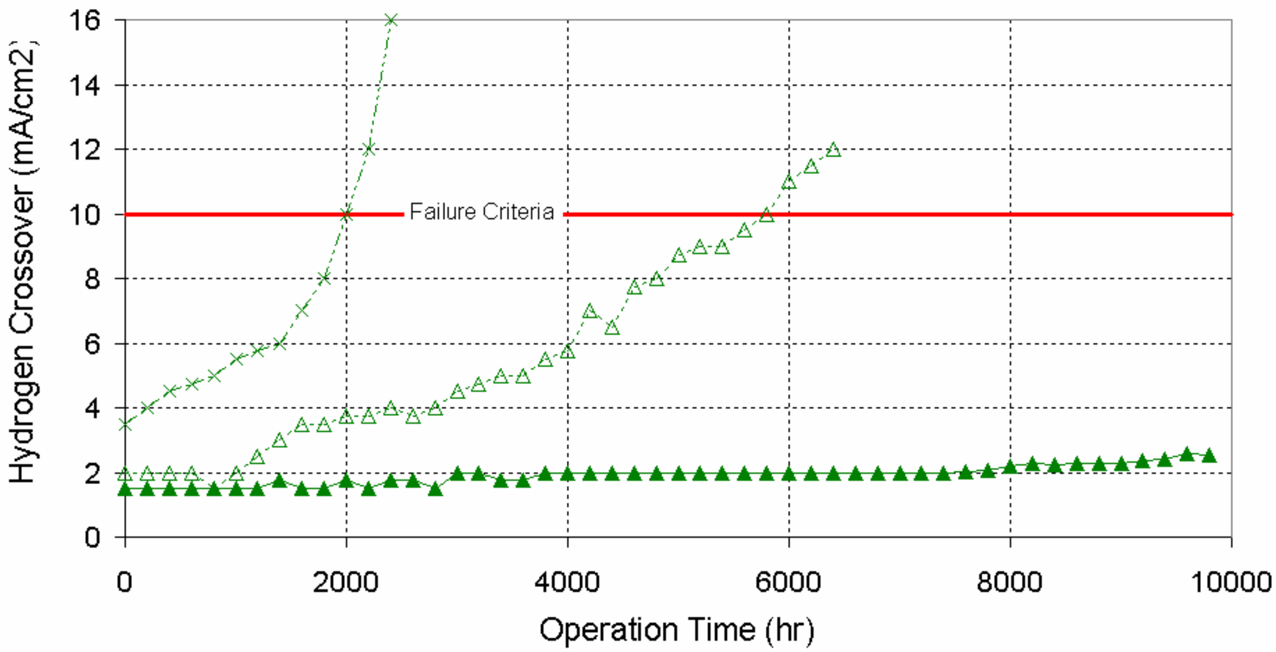
Impact of seal/membrane interface

Impact of seal design and materials on lifetime under accelerated conditions (same membrane and catalyst)



Data taken by Toshiba Fuel Cell Power Systems (H. Chizawa, A. Maekawa, and T. Aoki)

S. Motupally, “Fuel Cells Durability & Performance”, Knowledge Foundation, Miami, FL 2006

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Summary

HT accelerates chemical degradation of membranes. Mechanical degradation coupled chemical attack key for membrane durability.

At very low RH, chemical degradation rates decrease.

Impact of Pt dissolution on performance and membrane durability could be key for design of advanced HTM membranes.

Hydrocarbon membranes have low chemical degradation rates under OCV conditions. Improvement in mechanical properties key.