FUEL CELL ELECTRODE OPTIMIZATION FOR OPERATION ON REFORMATE AND AIR

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DOE 2002 Review
Fuel Cell for Transportation Program

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Approach

I. Cathode:

1. Detailed studies of catalyst layer structure and function
2. Screening to determine best available catalysts
3. Develop new diagnostic tools
4. Create physical property databases

II. Anode:

1. Continue development of advanced approaches to CO tolerance
2. Determine effects of low levels of H_2S (ppb) on FC performance

III. Collaborations with industries and government laboratories

Industrial Outreach and Collaborations

Los Alamos

Donalson (CRADA/Feb. 02): *Ambient Air Impurities*

DuPont (CRADA/ March 02): *Advanced MEA Development*

Superior MicroPowders: *Advanced Cathode Catalysts Evaluation*

OMG: *Advanced FC Catalysts Evaluation*

Brookhaven NL: *Low Loading Anode Pt Catalyst Assessment (R. Adzic)*

Nuvera: *Exploring true Reformate/FC test program*

Cabot: *Evaluation of Advanced Carbon Materials for Fuel Cells*

Cathode Development: Goals and Approach

Overall goal: Achieve maximum current density at 0.8 V

Approach:

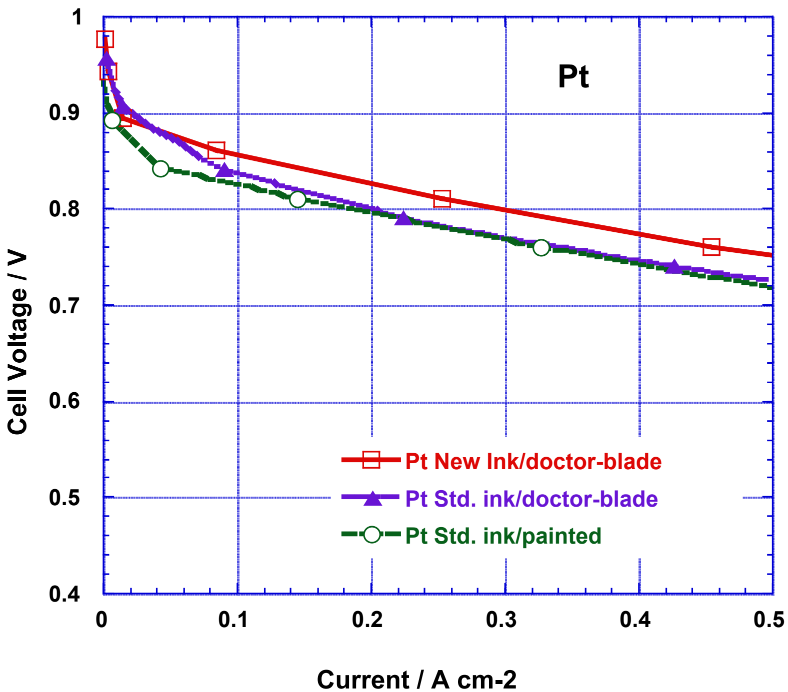
- **Improve cathode catalysts**
  - **Work with vendors to develop/test new catalyst formulations**
  - **Develop in-house capability to prepare highly dispersed catalysts**

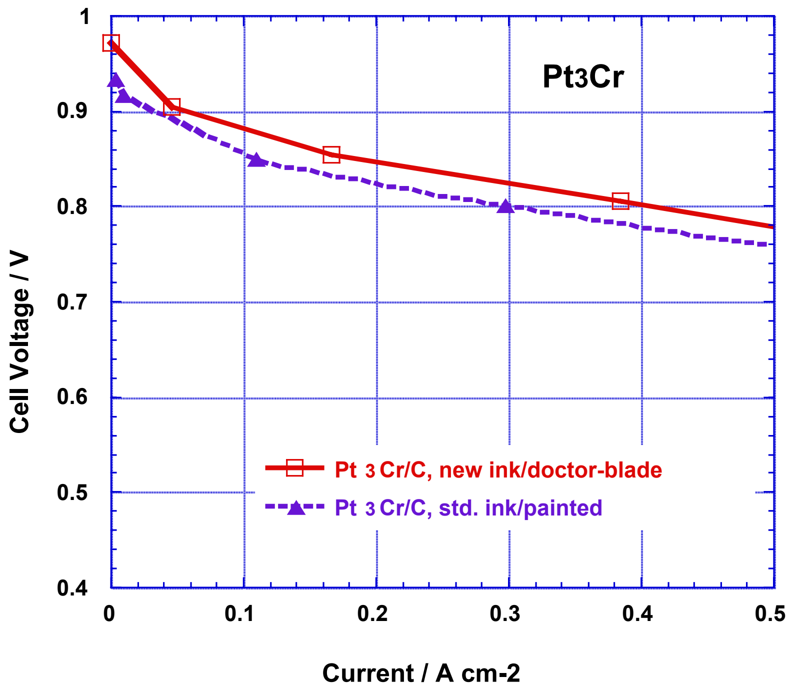
- **Develop new catalyst ink formulations and MEA preparations**
- **Study the dependence of catalyst layer structure on performance**
- **Studies of ambient air impurity effects on cathode (SO_2, NO_x , particulate impurity,etc.)**

Cathode Optimization: New Ink and Decal Preparation

FC Performance with H_2/air at 80°C

Milestone: Achieve 0.4 A/cm^2 at 0.8 V on H_2 with <0.25 mg Pt/cm^2 (Sept. 02)





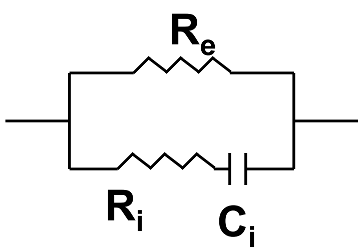
Cathode : 0.2 mg Pt/cm^2
Anode : 0.2 mg Pt/cm^2

New tool for developing optimized catalyst layers

Developed in BES Project * / Applied to the FC program

Method allows differentiation between electronic resistance (R_e) and ionic resistance (R_i) in the catalyst layer.

Measurements in a Catalyst/Nafion Composite Film



i= ionic
e= electronic

Constant current DC polarization → $V = i R_e$

AC impedance (high freq.) → $Z_{re} = (1/R_e + 1/R_i)^{-1}$

→

Example of a Result

Since R_e = 117 k ohm

and Z_{re} = 93 k ohm

then R_i = 465 k ohm

* A. Saab, F. Garzon, T. Zawodzinski. Accepted by *J. Electrochem. Soc*.

New tool for developing optimized catalyst layers:

Applications

Carbon materials courtesy of Cabot Corporation

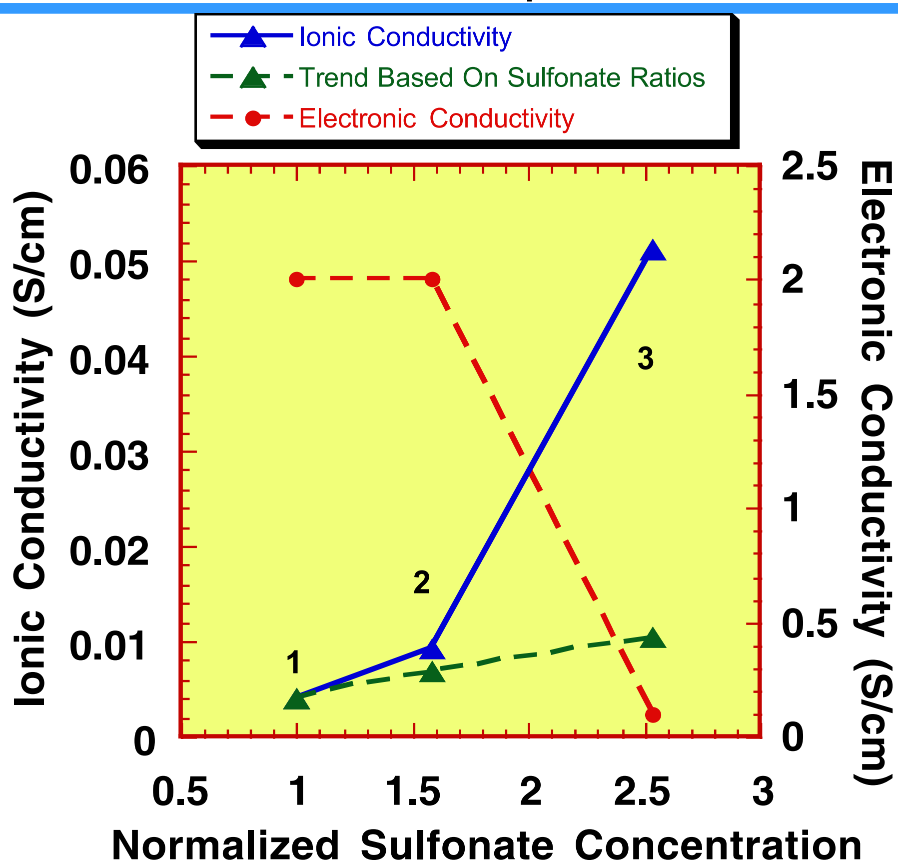


Fig. Ionic and electronic conductivities vs. normalized sulfonate concentration for composites made with phenyl sulfonic derivatized XC-72 carbon black

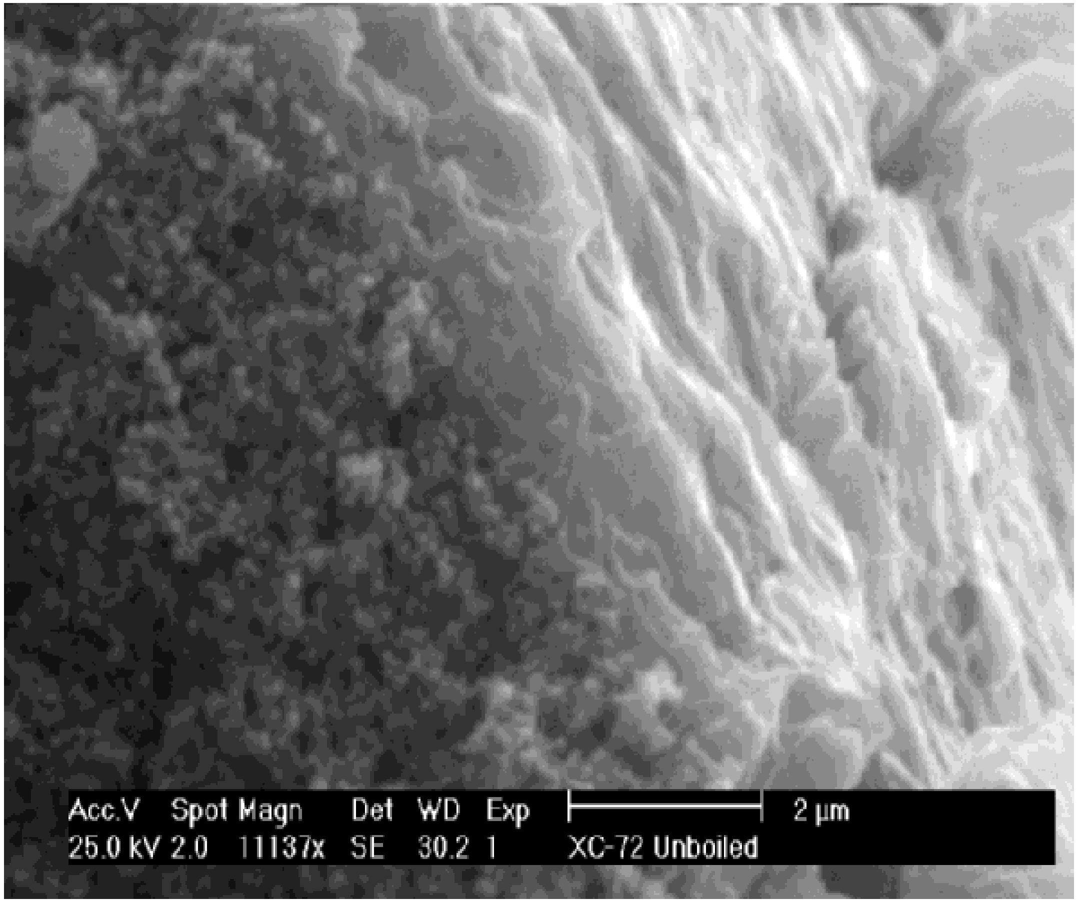
← Composite

1. **XC-72**
2. **4 w% phenyl sulfonic der. XC-72**
3. **10.7 w%phenyl sulfonic der. XC-72**

Other applications

- **Dependence of conductivities on MEA preparation variables**
- **Effect of impurities on CL conductivity**
- **Effect of hydration on CL conductivity (CL= catalyst layer)**

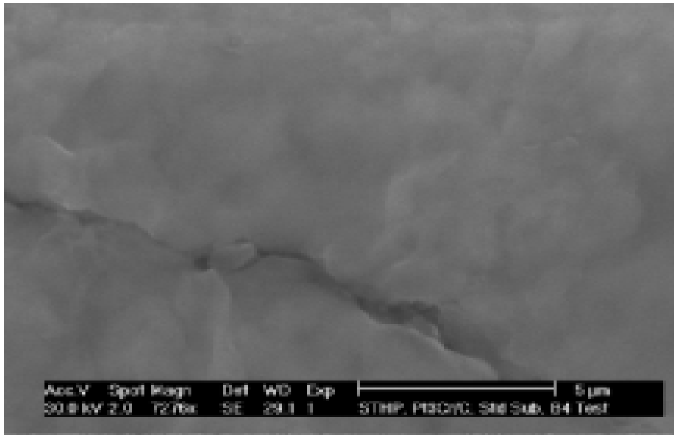
Cross-section of XC-72 Layer (29 wt% Nafion, unboiled)



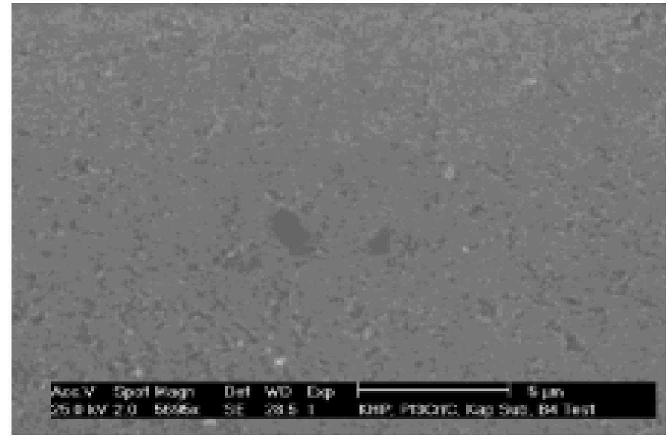
- Dense Ionomer skin on surface
- Skin decreases mass transport

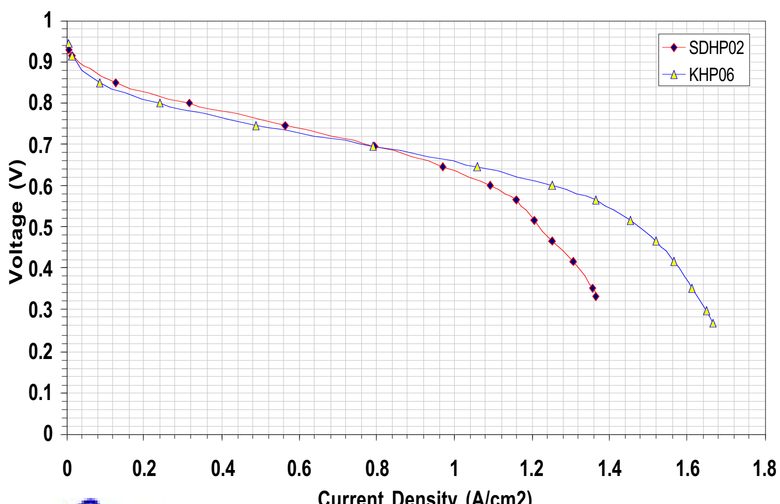
Impact of Decal Substrates: Teflon vs. Kapton

Teflon decal



Kapton decal



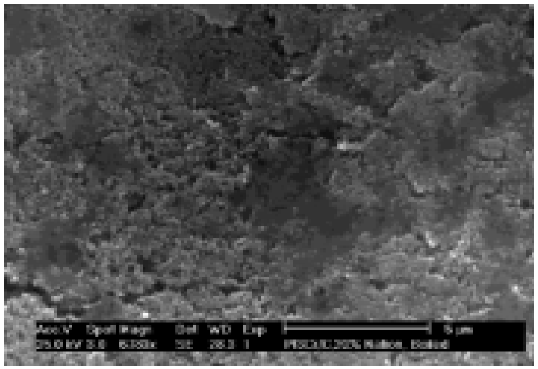


– Kapton decal greatly reduces skin

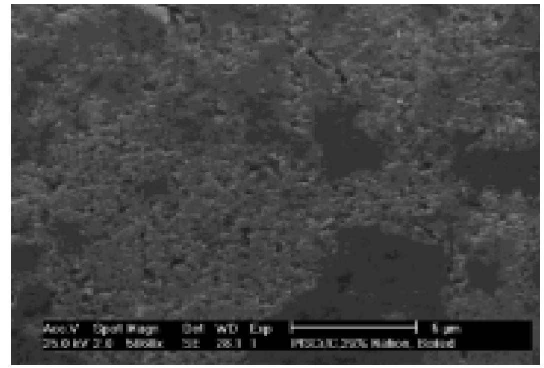
– Less porous catalyst layer made with Teflon yields lower limiting current

Impact of Nafion Content on Ionomer Skin

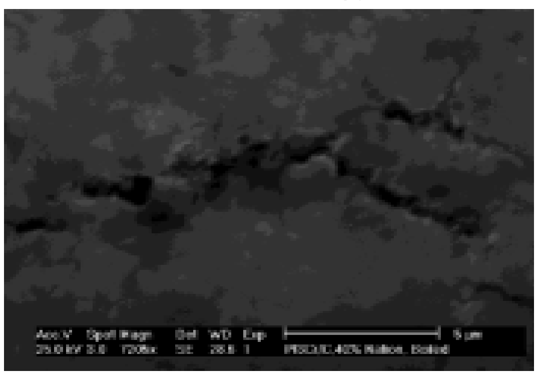
Nafion 20 wt.%



Nafion 29 wt.%



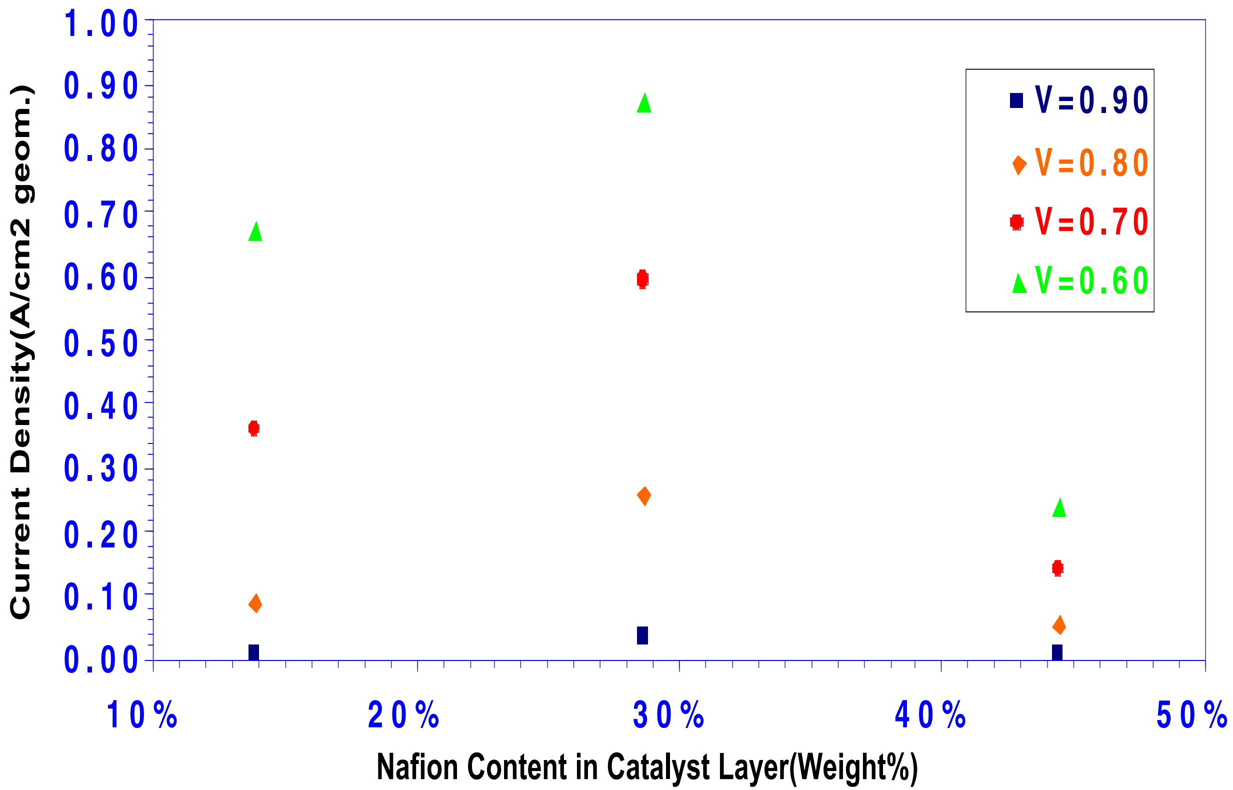
Nafion 40 wt.%



Nafion 69 wt.%

Pt_3Cr standard ink, hand painted on Teflon substrate, hot pressed and boiled
(See cathode performance results on the next slide)

Fuel cell performance as a function of cathode catalyst Nafion content



Best FC performance with approx. 29w% Nafion

Low Nafion content decreases H^+ conductivity

Too much Nafion limits mass transport and reduces electronic conductivity

Anode Development: Goals and Approach

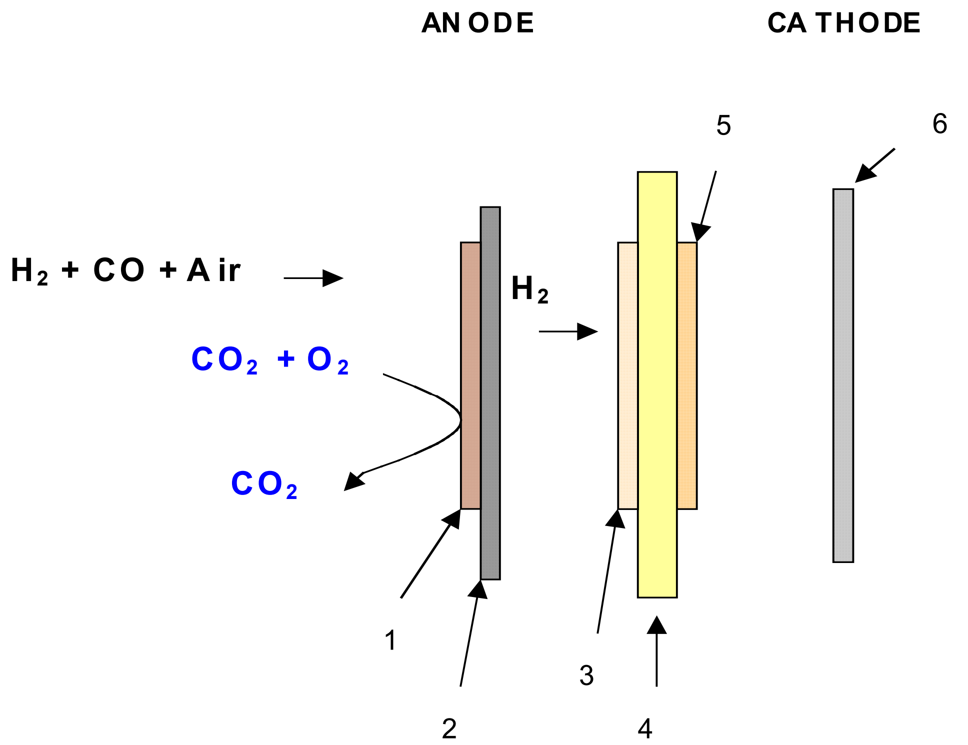
<u>Goals: Improve tolerance to CO and other impurities with lower precious metal loading</u>

Approach:

* **Continue development of reconfigured anode (RCA)**
* **Evaluate new catalyst materials with low Pt content.**
* **Evaluate effect low levels of H_2S on long term performance**

Fuel Cell Schematics with Reconfigured Anode:

Improve tolerance to CO by making air bleed more efficient



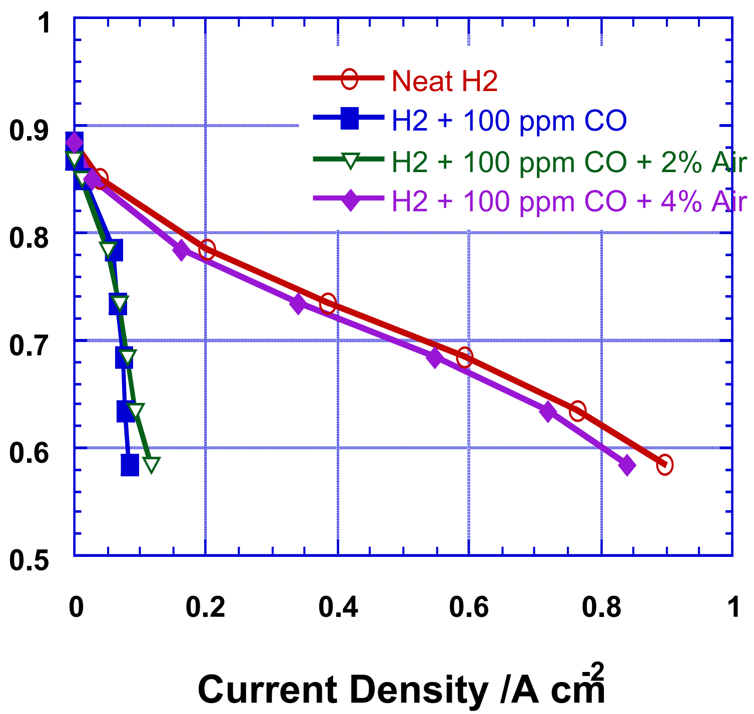
1. Non-precious metal chemical catalyst layer
2. Anode backing carbon cloth
3. Precious metal electrochemical catalyst layer
4. Polymer electrolyte membrane
5. Cathode electrochemical catalyst layer
6. Cathode backing carbon cloth

(See performance results on the next slide)

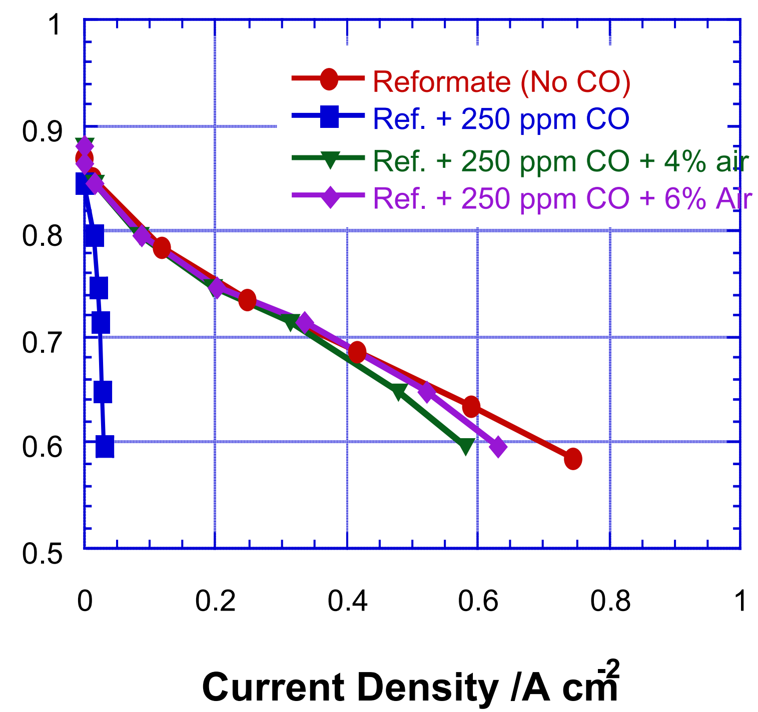
FC Performance with a Reconfigured Anode Type II at 80 °C

Non-Precious Metal Chemical Catalyst Layer at the Anode. 0.2 mg Pt/cm² at each electrode

H_2 / Air



Reformate / Air



Milestone in progress: Demonstrate full tolerance to 500 ppm CO in Reformate with <0.25 mg Pt/cm² (Jul 02)

Chemical catalyst at the backing

Co-Cryptomelane: KMn_8O_{16}

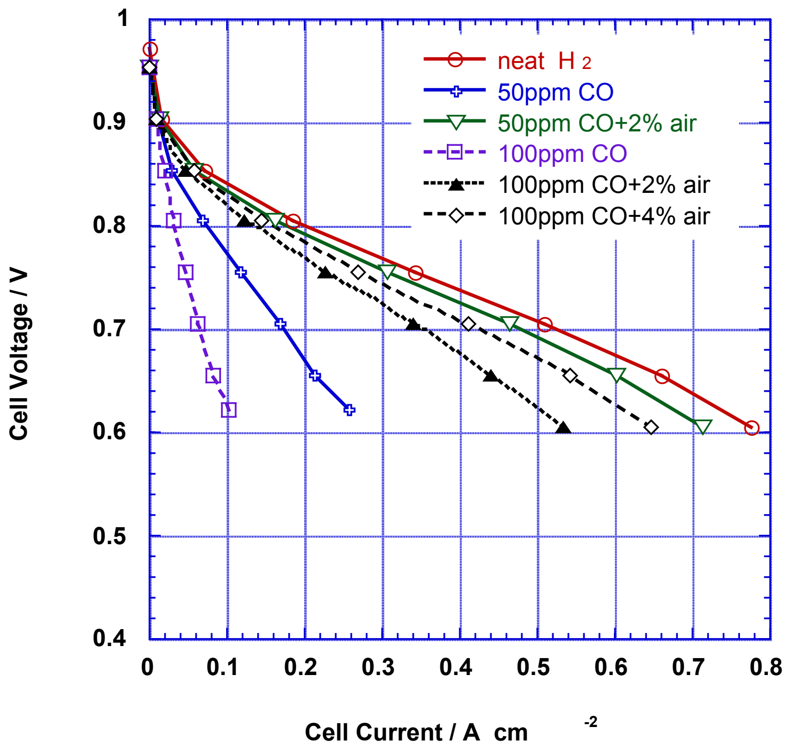
K^+ --> 1/2 Co^{2+} , 1/3 Co^{3+}

(porous structure)

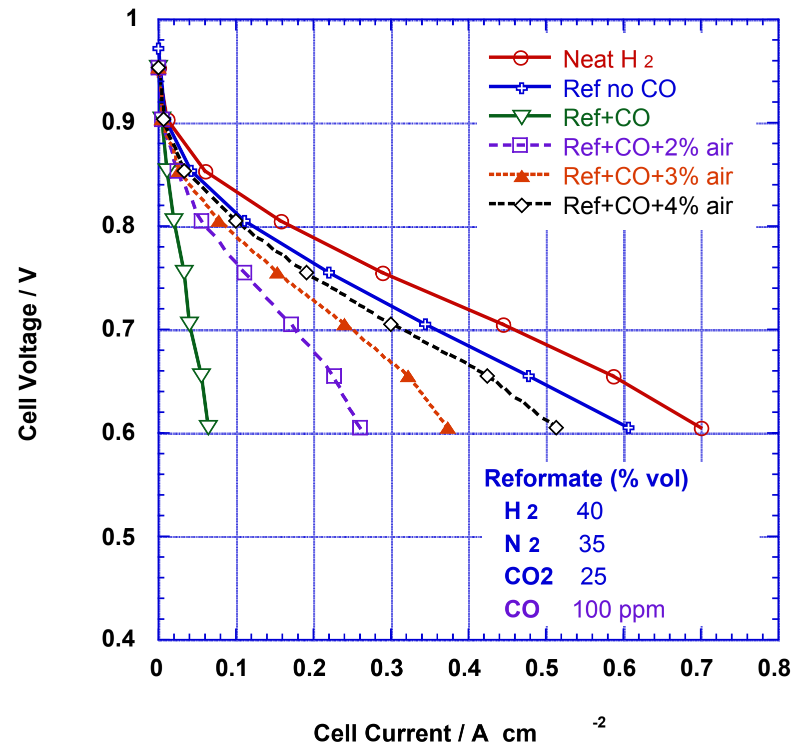
Low Pt Content Anode Catalyst for CO Tolerance

R. Adzic catalyst (BNL): 18 µg Pt /cm^2 (1% Pt-10% Ru/C)

Performance of a H2/air FC
with/without air bleed



Performance of a Reformate/air FC
with/without air bleed

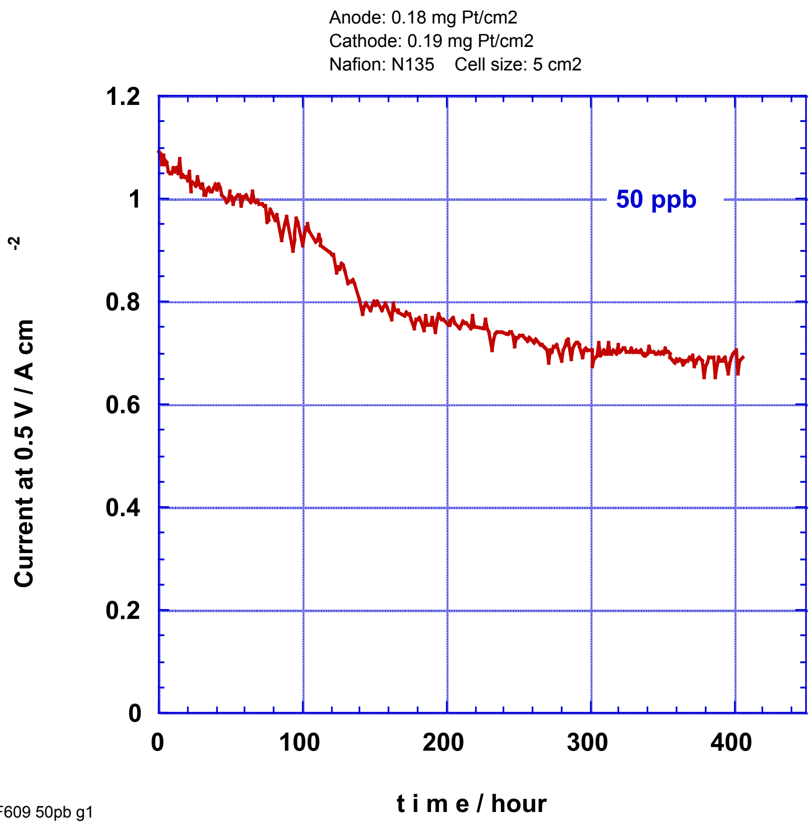


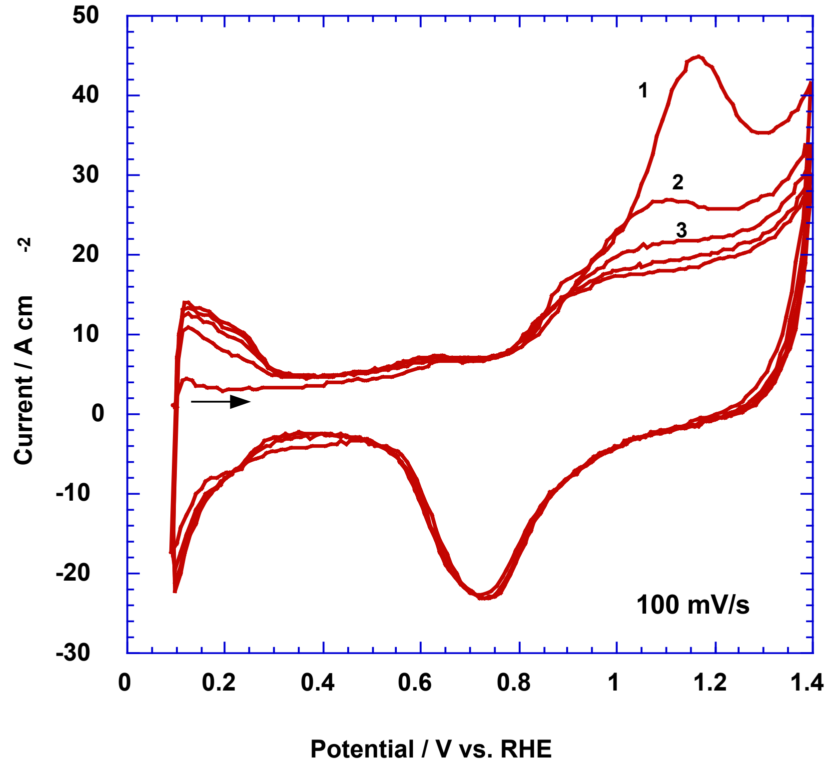
A: 0.2 mg Ru-Pt /cm^2 C:0.2 mg Pt/cm^2
1.5 stoich H_2 , T= 80 ^oC

Effect of 50 ppb H_2S anode impurity on H_2/Air FC Performance at 80 °C

Milestone: **report results with 50 ppb H_2S**

CV after exposure to H_2S cleans the Pt catalyst surface





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Fuel Cell Research

FY 2002 Progress

- **Substantial improvement in cathode performance with low Pt loading: 0.4 A cm^{-2} at 0.8 V**

  old: 0.4 mg Pt/cm^2 --------- new: 0.2 mg Pt/cm^2 (Pt_3Cr)

- **Significant decrease in anode loading needed for tolerance to 100 ppm CO:**

  old: 0.1 mg Pt/cm^2 --------- new: 0.02 mg Pt/cm^2 (R. Adzic catalyst)

- **Improvement in CO tolerance level with 0.2 mg Pt/cm^2 (in Reformate)**

  old: 100 ppm CO --------- new: 250 ppm CO

Future Work

Continue of work on:

- **Improve catalyst utilization**
  - ***New inks formulations***
  - ***New decal and MEA preparation techniques***
- **Improve CO tolerance**
  - ***Quantitative analysis on RCA operation***
  - ***Test new RCA materials and structures***
  - ***Measure durability of low Pt-content catalysts***
- **Evaluate modified carbon supports (Cabot)**
- **Examine structure-property relationship in the catalyst layer**
- **Study effect of ambient air impurities on FC operation**

Initiate work on:

- **FC Diagnostics with real Reformates**
- **Non-precious Metal Catalysts for FC Cathodes**