Effects of Impurities on Fuel Cell Performance and Durability

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Project ID#: FC29

Overview

- **Timeline**
  - Start: Feb. 15, 2007
  - Finish: Feb. 14, 2011
  - Completed: 25%
- **Budget**
  - Total Project Funding
    - DOE Share:
      - CU: $1,205,425
      - SRNL: $774,979
    - Cost Share:
      - CU: $295,101
      - John Deere: $193,745
  - Funding received in FY07
    - CU: $222,982
    - SRNL: $125,000
  - Funding for FY08
    - CU: $295,721
    - SRNL: $200,000

- **Barriers**
  - Fuel cells stacks do not maintain performance over the full useful lifetime of a vehicle.
- **Targets**
  - Test, analyze and characterize MEAs before, during and after operation
  - Develop electrocatalysts with reduced precious metal loading, increased activity, improved durability / stability and increased tolerance to air, fuel and system-derived impuritie
  - Develop sustainable MEA designs that meet all targets
- **Partners**
  - Clemson University
  - SRNL
  - John Deere

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Objectives

- **Investigate in detail the effects of impurities in the hydrogen fuel and oxygen streams on the operation and durability of fuel cells.**
  - CO, CO_2, NH_3, H_2O, HCs (incl. C_2H_4, C_2H_6, H_2CO, $HCOOH$), O_2, inert gases (He, N_2, Ar), Cl_2, and H_2S.
- **Determine mechanisms of impurity effects.**
- **Suggest ways to overcome impurity effects.**

Objectives – Year 1

- **Obtain and characterize components of MEA to be used (20% Pt/C, 30% Nafion/C, Nfn-Pt/C, Nafion membrane).**
- **Design and set up measurements of impact of impurities on MEA components.**
- **Install Fuel Cell Test Station.**
- **Calibrate FC Test Station measurements in “round robin” test of standard MEA with other DOE contractors.**
- **Start characterization of effects of CO and NH_3.**

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Revised Milestones

Qtr	FY	Materials Acquisition /Prep./Modeling	Pt Study (Pt/C, Nafion/Pt/C)	Nafion Study (Nafion/C, Nafion/Pt/C and Nafion membrane)	PEMFC Performance Testing
1	**2007**	Materials purchase (Pt/C, PtRu/C, Nafion, gas mixtures)	training of student	training of student	Purchase of PEMFC
2	**2007**		Characterization of Pt/C	Characterization of Nafion/C	Installation of gas mix. sys.
3	**2007**		Constr. of H_2-D_2 and H_2-O_2 reaction system, start study of CO	Modif. of Nafion acidity test system. start study of NH_3	Design of test protocols
4	**2008**	Prep. of Nafion membranes for conductivity meas.	Integration of mass spec to reaction/ads. system, cont. CO study	Purchase of imped. meas. system, cont. study of NH_3	Finalizing test protocols, installation of FC Test Station, MEA preparation
5	**2008**	Prep. of Nafion membranes	**Effect of CO,**	**Effect of NH_3**	Round robin test of benchmark MEA, **Effect of CO**
6	**2008**		**Effect of CO, Effect of NH3**	**Effect of NH_3 Effect of CO**	**Effect of NH_3**
7	**2008**		**Effect of CO_2**	**Effect of CO_2**	**Effect of CO_2**
8	**2009**	**Development of poisoning model**	**Effect of Ethylene Effect of Ethane**	**Effect of Ethylene Effect of Ethane**	**Effect of Ethylene Effect of Ethane**
9	**2009**	**Go-No Go Decision**	**Go-No Go Decision**	**Go-No Go Decision**	**Go-No Go Decision**

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Approach

Fundamental Studies

Investigate impact of impurities on Pt/C , Nafion/C, and Nafion

Fuel Cell Studies

Investigate poisoning effects of Impurities on fuel cell performance

Delineation of mechanisms for poisoning by gas impurities

Development of strategies to reduce the detrimental effect of impurities

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Experimental

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- Phys. & Chem. Characterization
  - BET (Pt/C, Nafion, Naf-Pt/C)
  - XRD (Pt/C, Nafion, Naf-Pt/C)
  - SEM/TEM (Pt/C, Nafion, Naf-Pt/C)
  - EDS (Pt/C, Nafion, Naf-Pt/C)
  - FT-IR (Pt/C, Nafion, Naf-Pt/C)
  - H_2 Chemisorption (Pt/C, Naf-Pt/C)
  - Acid site titration (Nafion, Naf-Pt/C)
  - NH_3 ads. to meas. BA sites (Nafion, Naf-Pt/C)
- *Reaction Characterization*
  - *H_2-D_2* (Pt/C, Naf-Pt/C)
  - *H_2-O_2* (Pt/C, Naf-Pt/C)
  - Model BA-catalyzed reaction (Nafion, Naf-Pt/C)
- *Conductivity Measurement*
  - Impedance analysis (Nafion, Naf-Pt/C)

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<u>Gas Impurity Mixture Generator</u>
Kin-Tek mixture generator
Up to 48 mixed impurities
Up to 500 sccm

<u>FC Single Cell Test Station</u>
Arbin FCTS 200H
Max. Power: 200 W
Max. Temp.: 130°C

Temperatures	80° C
Pressure	2 bara (P_a=P_c)
Humidity	100 % RH anode, 50 % RH cathode
Stoichiometry (A/C)	H_2/Air = 1.1/2.5 @ 1000 mA/cm^2
Loading	Anode 0.1 mg Pt/cm^2 (20 wt% Pt-C)
	Cathode 0.3 mg Pt/cm^2 (40 wt% Pt-C)
Electrolyte	Nafion® 212
Cell Area	50 cm^2
Current density	1000 mA/cm^2

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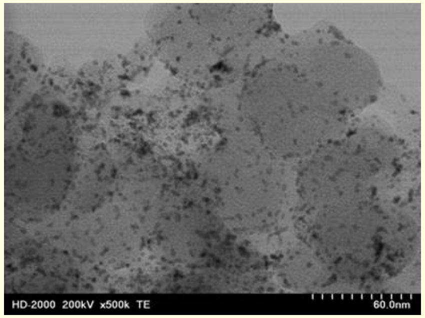
Experimental: *Materials**

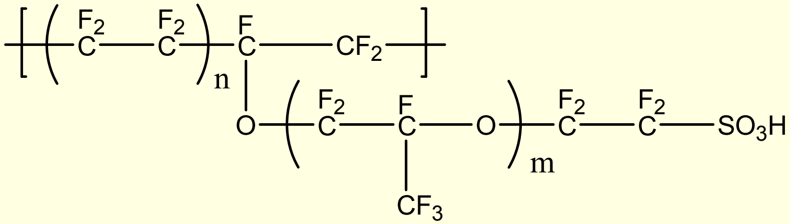
- **Anode: 20 wt% Pt/C (E-TEK)**
  - **Pt Particle Size: 22 Å (Co.)**
  - **BET Surface Area: 112 m^2/g (Co.)**
- **Cathode: 40 wt% Pt/C (E-TEK)**
  - ***Pt Particle Size: 29 Å (Co.)**
  - ***BET Surface Area: 100 m^2/g (Co.)**

Fresh Pt/C



Element	Wt. %	Atom. %
C K	84.8	96.8
O K	2.5	2.1
S K	0.4	0.2
Pt M	12.4	0.8
Total	**100**	**100**

- **5 wt% Nafion EW 1100 Solution (Ion-Power)**



- **Carbon Black Powder (XC-72R)**
  - **BET Surface Area: 250 m^2/g (Co.)**
- **MEAs (E-TEK)**
- **Nafion ® 212 Membrane EW 1100 (Du Pont)**

BET Surface Area:

- **C Support: 226 m^2/g**
- **20 wt% Pt/C: 112 m^2/g**
- **30 wt% Nafion/C: 59 m^2/g**
- **30 wt% Nfn-Pt/C: 62 m^2/g**

Acid Site Density:

30 wt% Nafion/C: 270 μmol/g
30% Nfn-Pt/C: 227 μmol/g

** Commercial Products*

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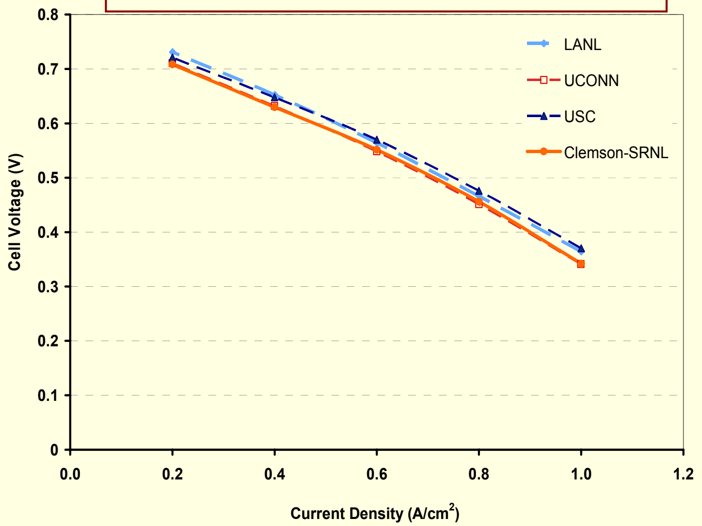
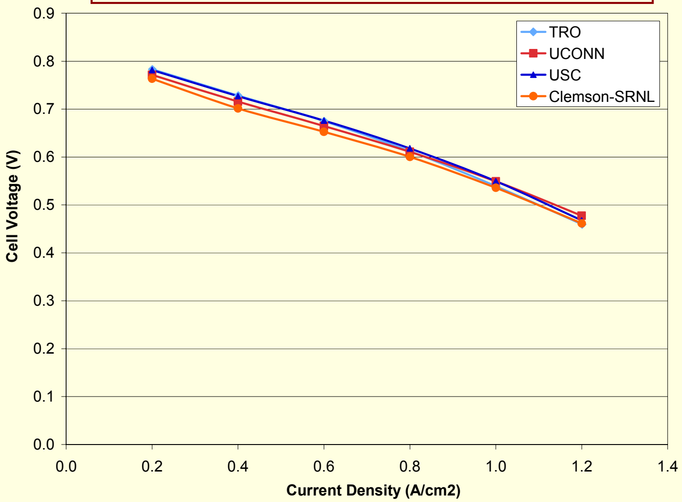
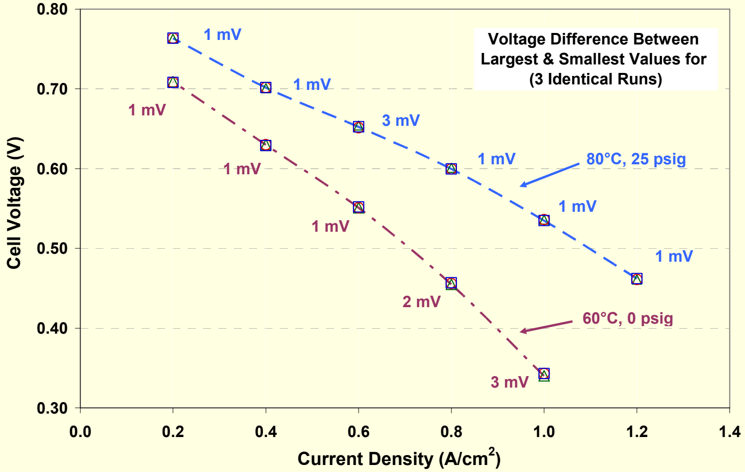
USFCC Round Robin: *SRNL FC Results*

60oC, 0 psig, 100% RH



80oC, 25 psig, 100% RH





- **Excellent reproducibility** was found between labs and FC test stations.
- **Reproducibility** of the SRNL **FC test station** was excellent.

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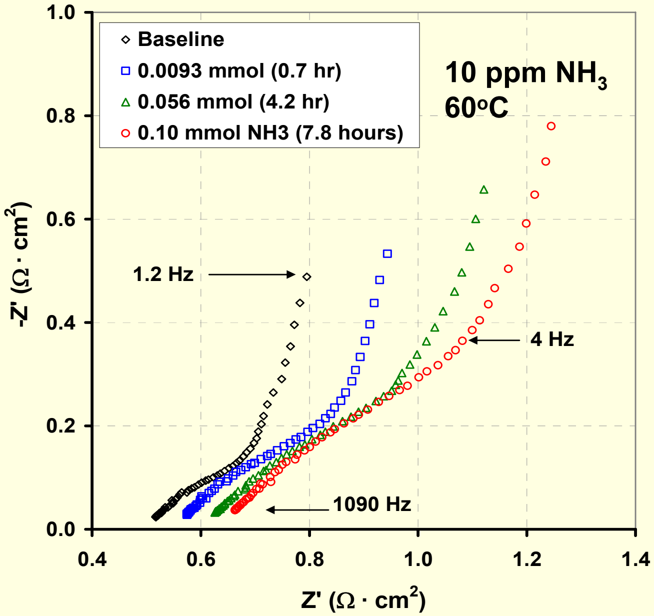
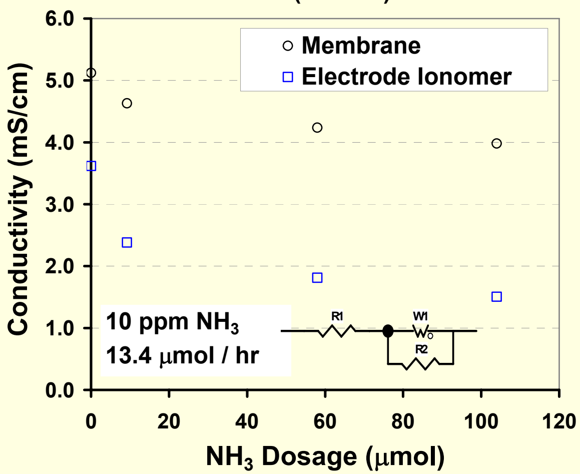
Electrochemical Impedance Spectroscopy (EIS):

10 ppm NH_3 Effect on Membrane & Ionomer @ 60°C





- The <u>baseline</u> run before poisoning is shown in black.
- Area corrected <u>membrane resistance</u> is given by the high frequency intercept with the x-axis.
- The <u>ionomer resistance</u> is proportional to the length of the "45°" line segment between 1090 Hz and ca. 4 Hz.
- This analysis method shows that <u>both</u> the membrane and electrode ionomer <u>resistances increase</u> during NH_3 poisoning.

Ion Power MEA (0.3/0.3 mg Pt)
Working Electrode – 10 ppm NH_3 in Ar at 500 sccm (13.4 μmol / hr); 75% RH
Ref. / Counter Electrode - H_2 at 500 sccm ; 75% RH
Potential Bias (11 mV vs. OCV)
Perturbation (10 mV)
Inductance Correction (0.36 mH)

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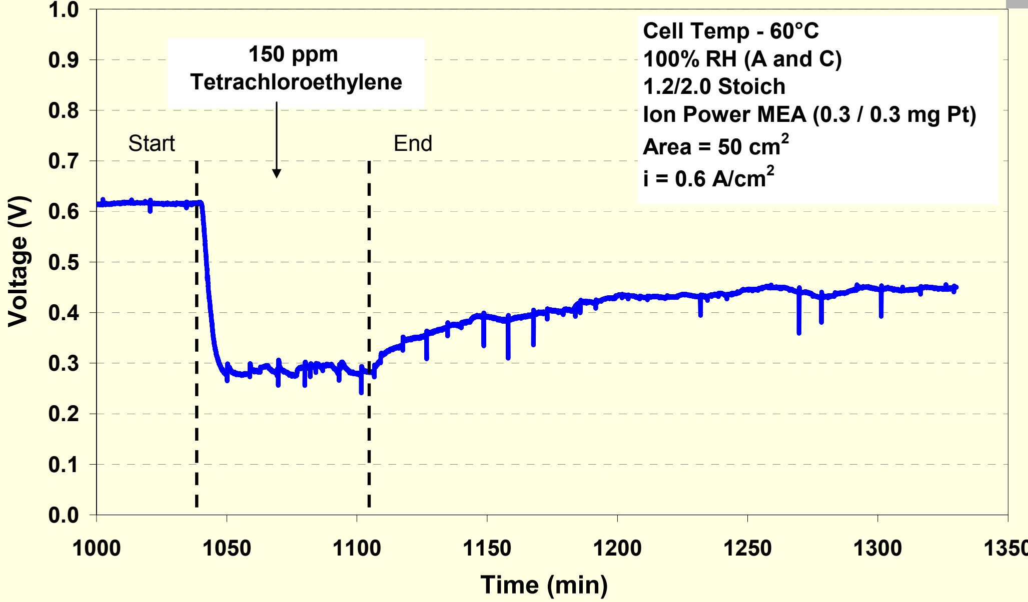
PEMFC: Effect of Tetrachloroethylene @ *150 ppm*



- The impurities generator at SRNL can simulate many different individual contaminants or contaminant mixtures.
- As a preliminary checkout of the system, poisoning of a 50 cm^2 cell with <u>150 ppm of tetrachloroethylene</u> (dry), a representative chlorinated hydrocarbon typical of many degreasing agents, was carried out.
- Loss of more that <u>50% of the cell potential</u> resulted within a few minutes to give a new pseudo-steady-state operating potential. The cell was able to recover 50% of its loss when the impurity was stopped.

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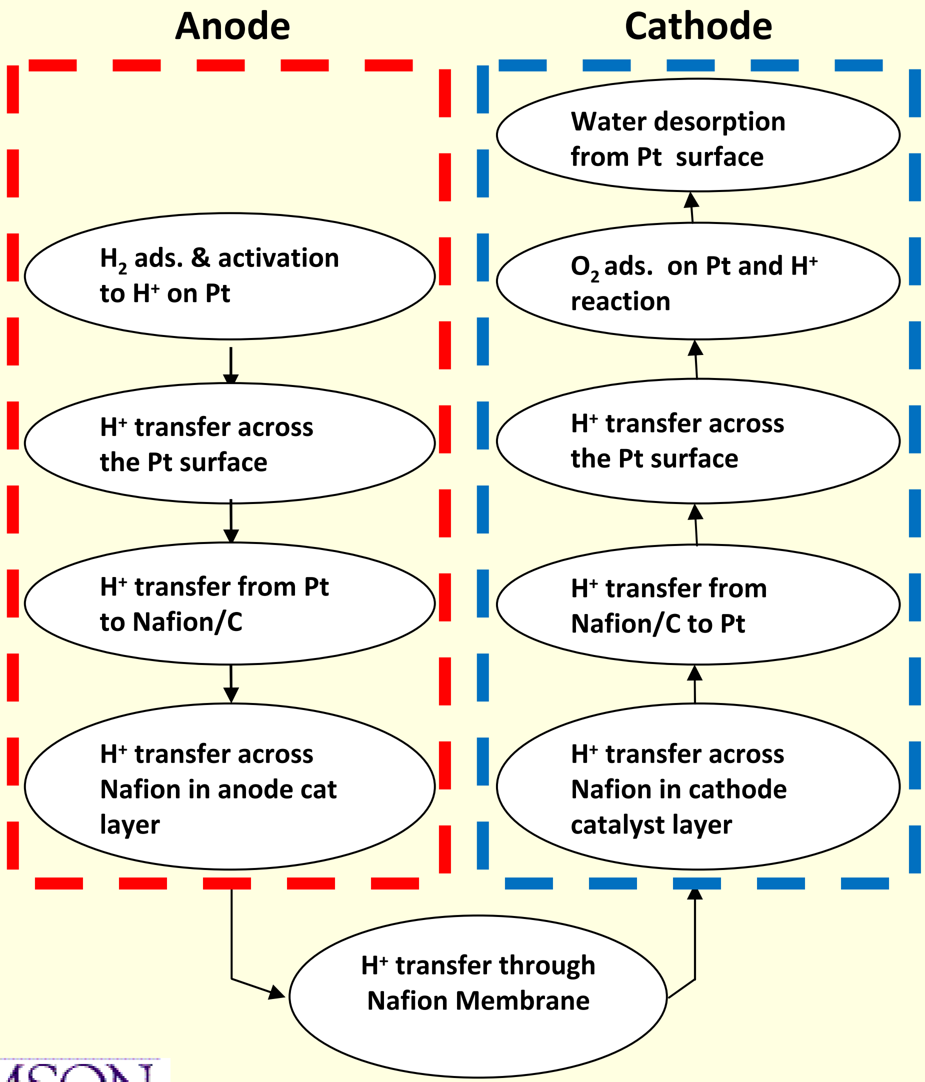
Rate Steps during FC Operation



Use to model effect of poisons on fuel cell operation based on direct measurements.

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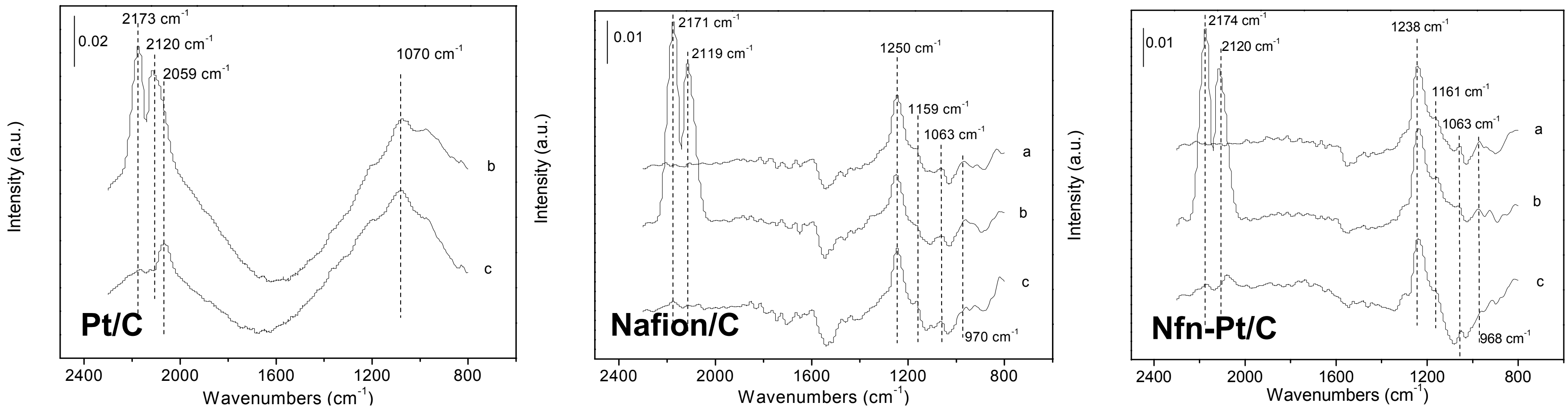
DRIFTS spectra of CO on Nafion/C, Nfn-Pt/C, and 20% Pt/C:

a: fresh sample*; b: in flowing 4% CO in H_2; c: followed by H_2 purge at 80℃



- ❑ **CO adsorbs on Pt/C as linear CO.**
- ❑ **CO does not adsorb on Nafion/C, which may explain the slight effect of CO on the activity of Nafion/C for esterification.**

IR band assignment

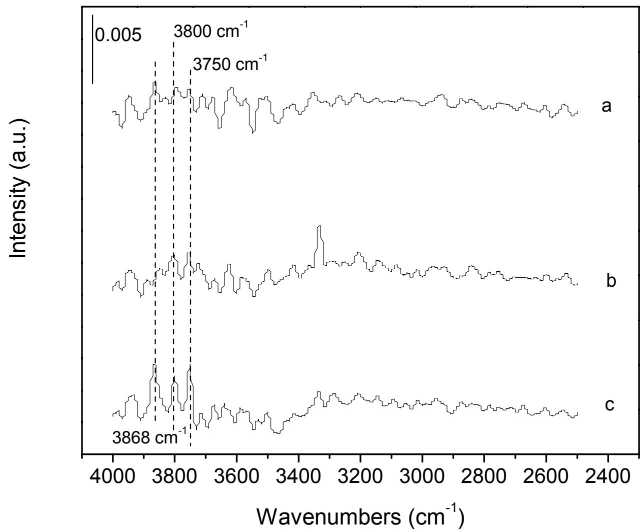
Wavenumber/cm^{-1}	Surface species
2171, 2119	gas phase CO
2059	linear CO
1250	CF_2 asymmetric stretching
1159	CF_2 symmetric stretching
1070	COH_x
1063	S-O symmetric stretching
970	C-O

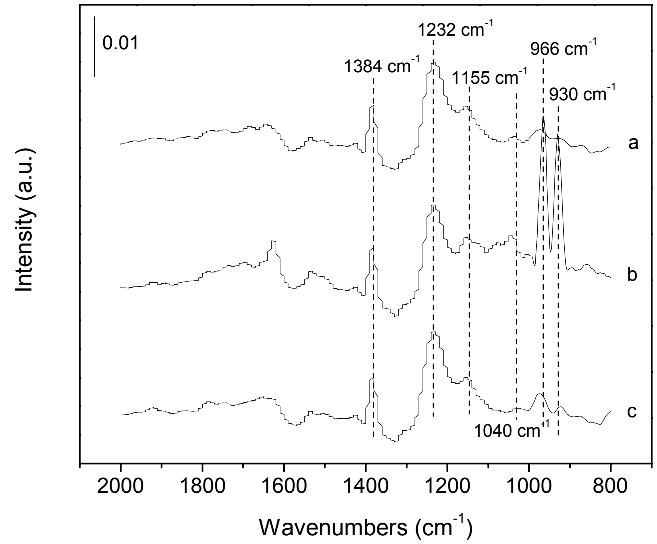
- ❑ **The shift in wavenumber of CF_2 to lower frequency for Nfn-Pt/C indicates there is interaction between Pt and Nafion.**
- ❑ **CO adsorbs less and more weakly on Nfn-Pt/C, perhaps due to this interaction.**
- ❑ **COH_x species appear to be formed on Pt/C in the presence of CO and H_2.**
- ❑ **CO and COH_x species block Pt sites required for H_2 adsorption, resulting in lower performance of the PEMFC.**

* The fresh samples were treated in H_2 at 80 ℃ for 3 hours prior to IR.

DRIFTS spectra of NH_3 on Nafion/C:

a: fresh Nafion/C; b: flowing 750 NH_3 in H_2; c: after He purge at 80℃ .





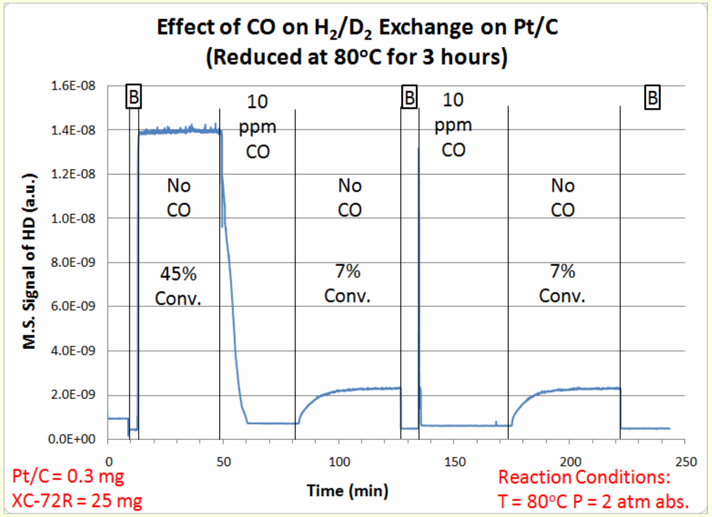
IR band assignment

Wavenumber/cm^{-1}	Surface species
3868, 3800, 3750	NH_4^+
1384	CF_2 asymmetric stretching
1232	CF_2 asymmetric stretching
1155	CF_2 symmetric stretching
1040	S-O symmetric stretching
966, 930	gas phase NH_3

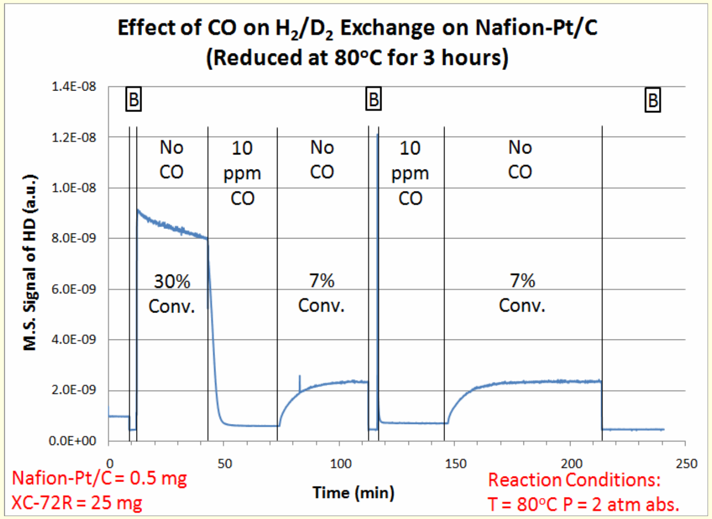
- **Peaks assigned to NH_4^+ can be observed, indicating that NH_3 absorbed on the Bronsted acid sites of Nafion forming NH_4^+.**
- **The formation of NH_4^+ reduces the proton conductivities of the Nafion membrane and the anode catalyst ionomer layer.**

Effect of 10 ppm of CO on H_2 Activation

Pt/C



Nfn-Pt/C



- ❑ **Pt/C is very active for H_2 dissoc. (equilibrium reached with only 0.3 mg of catalyst).**
- ❑ **Pt/C is effectively poisoned in 10 min, suggesting that practically every CO adsorbs.**
- ❑ **Nafion-Pt interactions cause H_2 dissociation to be somewhat inhibited on Nfn-Pt/C.**
- ❑ **Nafion-Pt interactions may be due to interactions with sulfonic acid groups/CF_2.**
- ❑ **Presence of CO, even at 10 ppm, stops H_2 activation.**
- ❑ **Poisoning effect is partially reversible at 80°C within 20 min, but most CO strongly bound.**

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20 wt% Pt/C = 677 μmol Pt_s/g-cat. For 0.3 mg Pt/C = 0.20 μmol Pt
Flow of 10 ppm CO = 0.041 μmol CO/min

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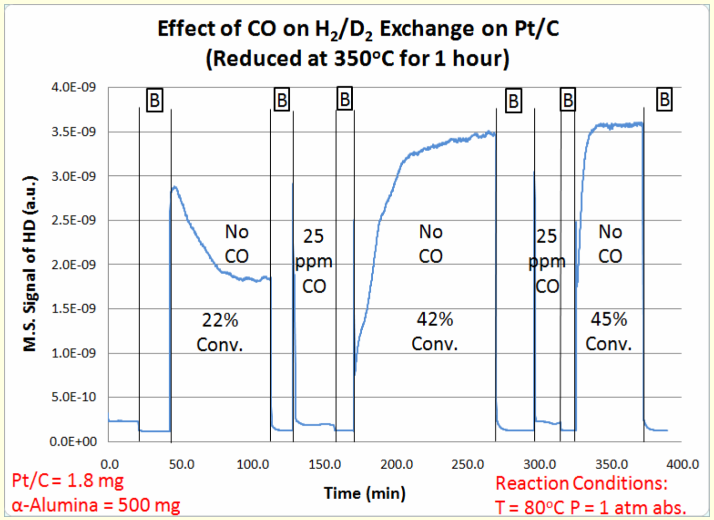
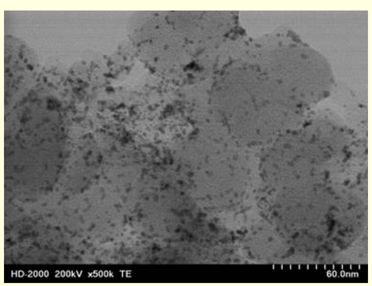
Effect of 25 ppm of CO on H_2 Activation

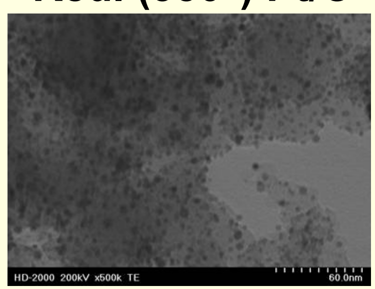


Fresh Pt/C



d_{Pt} = 2.9 nm

Red. (350°) Pt/C



d_{Pt} = 4.8 nm

- **If Pt/C is <u>reduced at 350°C</u>, the Pt particles sinter and the activity is less since the amount of exposed Pt surface atoms is less.**
- **The Pt particle diameters increase from 2.9 to ca. 4.8 nm.**
- **25 ppm CO also results in total loss of activity.**
- **However, for these larger particles of Pt,**
  - **there is a total recovery of activity within 10-25 min. (no irrev. ads. CO).**
  - **increased H_2 activation is possibly due to Pt surface restructuring.**

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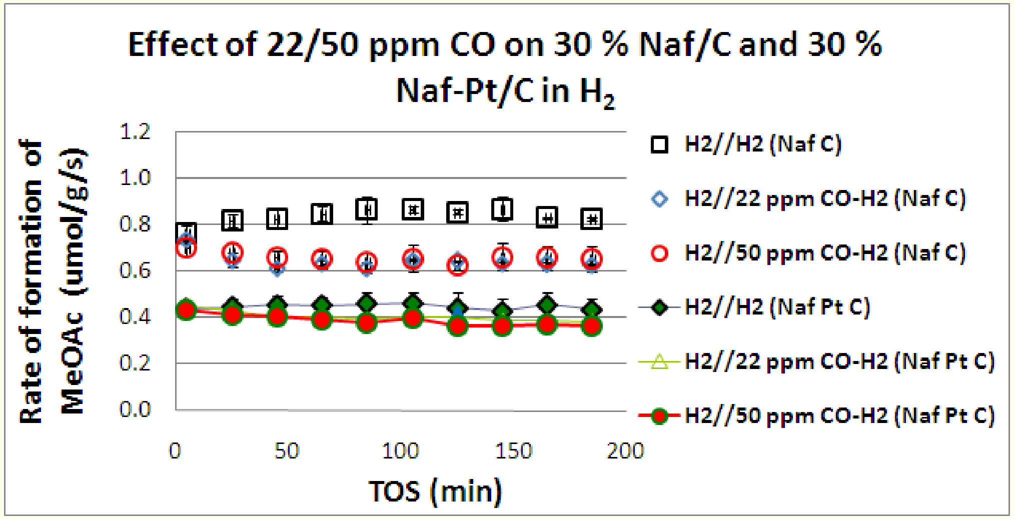
Effect of CO on Nafion/C and Nfn-Pt/C



Surface sites of Pt/C*

- 20% Pt/C = 677 µmol H/g

*Calc. from H_2 chemisorption

Proton site density*

- 30% Nafion/C = 270 µmol/g
- 30% Nfn-Pt/C = 227 µmol/g

*Based on S analysis

Esterification of HAc: Pres. = 1 atm (abs.),T = 80ºC, P_{MeOH} and P_{HAc} = 0.01 atm, Tot. flow rate = 100 sccm

- **The activity of 30% Nafion/C is greater than that of 30% Nfn-Pt/C. Pt appears to catalyze removal of some of the S when Nafion added to Pt/C [S content decrease while F content remains constant.**
- **The interaction of Pt with sulfonic acid groups/CF_2 may decrease the strength/number of acid sites in Nafion.**
- **CO has a small effect on the acidity.**
- **Even 22 ppm of CO causes the maximum effect.**

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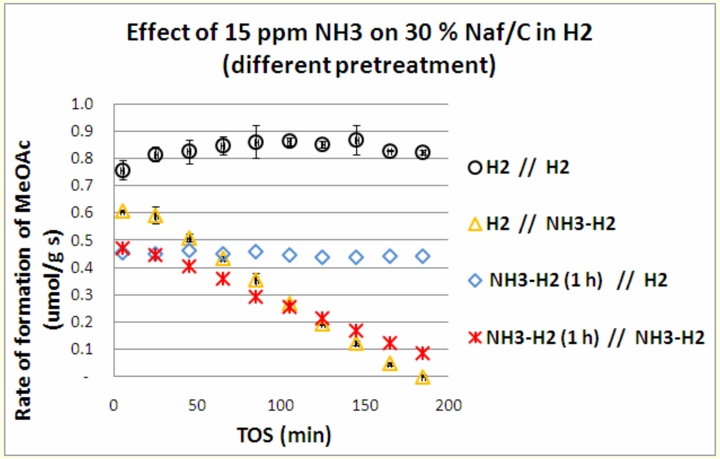
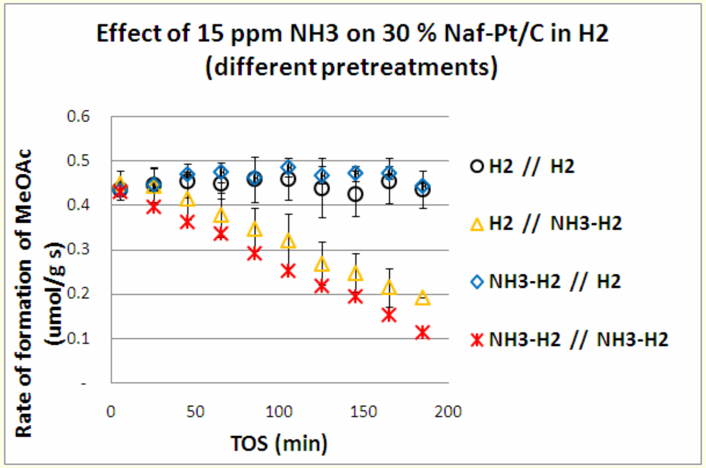
Effect of NH_3 on Nafion/C and Nfn-Pt/C





- The poisoning effect of NH_3 is cumulative and even at 15 ppm appears to be irreversible.
- The effect of NH_3 on the Brønsted acid sites on Nafion/C is more than that on Nfn-Pt/C.
- Pt may decompose NH_3 resulting in less poisoning of Nafion in Nfn-Pt/C.
- From NH_3 pulse chemisorption, it was found that NH_3 can adsorb on Pt/C leading to competitive adsorption of NH_3 on Pt/C and the sulfonic acid ions of Nafion.

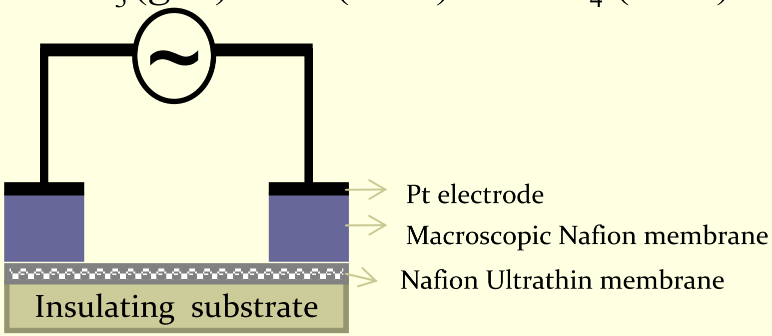
Esterification of HAc: Pres. = 1 atm (abs.),T = 80 C, P_{MeOH} and P_{HAc} = 0.01 atm, Tot. flow rate = 100 sccm

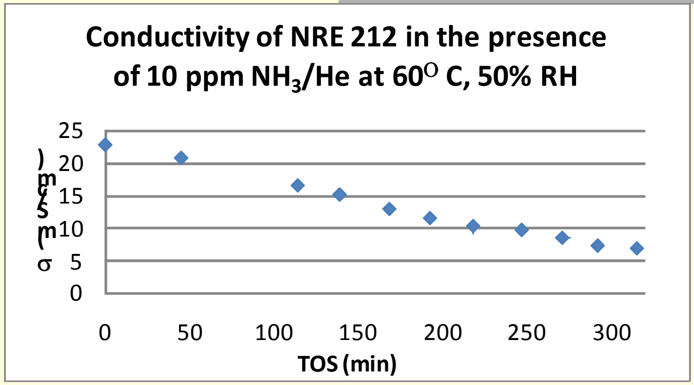
Proton site density*
- 30 % Naf/C = 270 μmol/g
- 30 % Naf-Pt/C = 227 μmol/g

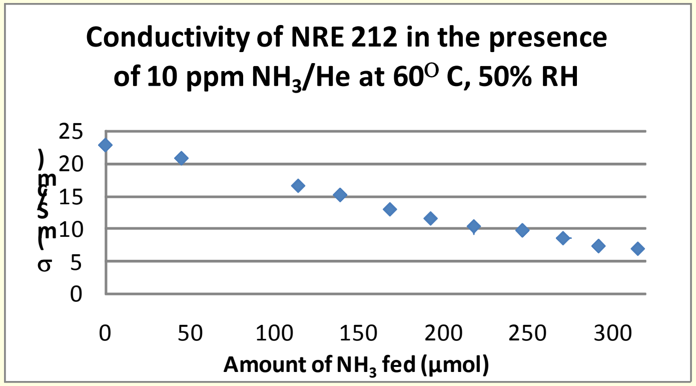
* Calculated by S elemental analysis

Impedance Measurement: *10 ppm NH_3 on Nafion 212*

$$NH_3(gas) + H^+(mem) \leftrightarrow NH_4^+(mem)$$







Conditions: T = 60°C, RH = 50%, 125 ppm NH_3 in He

- **Electrochemical cell designed to test ionic conductivity in the membrane**
- **Electrochemical Impedance Spectroscopy (EIS) is being used to test Nafion membrane and Nafion/C properties with poisoning**

- **σ (H^+ form) = 22.7 mS/cm**
- **σ (H^+ form from Springer model) = 22.3 mS/cm***
- **σ (NH_4^+ form) = 7 mS/cm**
- **σ of H^+ form Nafion® is ca. 3 times higher than NH_4^+ form which is in agreement with the value that Uribe et. al reported (3.8–4.2 times).****

**   T.E. Springer, J. Electrochem. Soc., 138, 2334 (1991).*
*** F.A. Uribe, T.A. Zawodzinski Jr., S. Gottesfeld, J. Electrochem. Soc. 149 (2002) A293.*

Fundamental Modeling Collaboration:

Clemson /SRNL/GreenWay Energy

- **Review Contaminant Model Literature**
  - Survey PEM literature to understand contaminant models.
  - Identify most relevant poisoning mechanism for CO and NH_3.
- **Develop First Principles Kinetic & Rate Expressions**
  - Create model as a tool for understanding *ex-situ* data.
  - Relate *ex-situ* and *in-situ* results.
- **Predict Results for Fuel Cell Testing**
  - Use comprehensive contaminant model to predict cell test results.
- **Program Model Code**
  - Give researchers direct access to model predictions in an easy to use format such as Maple or Matlab.

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Future Work (FY08-FY09)

- Activities
  - Complete studies of the effects of CO, NH_3, CO_2, ethane, and ethylene on fundamental processes and fuel cell performance.
  - Develop model for incorporating fundamental results to predict FC behavior.
  - Determine how well the measurement of effects on FC components predict FC performance.
- Upcoming Milestones
  - Complete fundamental studies of effects of CO, NH_3 , CO_2, ethane and ethylene on Pt/C, Nafion/C, and Nafion membrane.
  - Complete FC runs of effects of CO, NH_3 , CO_2, ethane and ethylene on FC performance.
- Decision Points
  - Go-No Go decision at end of 2^{nd} quarter FY 2009

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Summary

- Project started in Feb. 2007.
- MEA components acquired and characterized March-Oct. 2007.
- FC test station installed & operational in Nov. 2007
- Fundamental studies of CO indicated how Pt surface covered with CO prevents completely H_2 activation even at 10 ppm.
- Larger Pt particles appear to adsorb CO more reversibly with some surface restructuring likely.
- Pt interacts with Nafion in Nfn-Pt/C and appears to cause some decrease in S content.
- NH_3 at 10 ppm accumulates on the proton sites of the Nafion membrane decreasing proton conductivity >3X.
- Pt helps to protect Nafion from NH_3, but decomposed products may interact with organics to deactivate proton sites.
- Round Robin FC MEA test completed Jan. 2008 with excellent match.
- FC tests carried out for NH_3 and tetrachloroethylene.
- FC used to perform Electrochemical Impedance Spectroscopy to analyze conductivities, membrane performance and catalyst performance.