2011 U.S. DOE Hydrogen Program Annual
Merit Review and Peer Evaluation

Effects of Impurities on Fuel Cell Performance and Durability

J.G. Goodwin, Jr. (P.I.), Jack Zhang, and K. Hongsirikarn,
Clemson University

Hector Colon-Mercado (Speaker),
Michael Martinez and and Scott Greenway
Savannah River National Lab

Peter Finamoore
John Deere, Advanced Energy Systems Division

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Project ID: FC046

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Overview

- **Timeline**
  - Start: Feb. 15, 2007
  - Finish: Feb. 14, 2011
    NC ext. Sept. 30, 2011
  - Completed: 90%

- **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 FY10
    - CU: *$277,411*
    - SRNL: *$67,632*
  - Funding for FY11
    - CU: *$236,433*
    - SRNL: *$140,108*

- **Barriers**
  - **A. Durability:** Durability of fuel cell stacks, which must include tolerance to impurities and mechanical integrity, has not been established. Tolerance to air, fuel and system-derived impurities (including the storage system) needs to be established.

- **Targets**
  - **Transportation Fuel Cells**
    - Durability with cycling: 5000 h by 2015
  - **Stationary PEM Fuel Cell Power Systems:**
    - Durability @ <10% rated power degradation: 40,000 h by 2011

- **Partners**
  - Clemson University
  - SRNL
  - John Deere

Relevance

Objectives

- **PROJECT 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 2010-11**
  - Phenomenological Measurements on FC Components
    - Complete the investigation in detail of the effects of Nafion® and %RH on hydrogen activation on Pt in the absence and presence of CO poisoning.
    - Complete the study of the effect of perchloroethylene on H_2 activation and hydrogen surface coverage of Pt/C a FC conditions.
    - Finalize the study of H_2O_2 degradation of Nafion® membranes.
  - Fuel Cell Performance Studies
    - Complete the investigate of the effects of the Cl-containing hydrocarbon (PCE) and THF.
    - Complete long term study of the effect of NH_3 poisoning per DOE request.
    - Complete CO poisoning experiments to correlate and compare results from PEM fuel cell test at SRNL to the results from H_2 activation studies at Clemson.

Technical Approach

Phenomenological Studies

Investigate impact of impurities on Nafion-Pt/C, Pt/C , Nafion®/C, and Nafion® membranes

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

Completed

~~AAA~~ Modified & Completed

Approach

Milestones

In Progress

Qtr	Mat. Acquis./Prep.	Pt/C Study	Nafion Study	PEMFC Testing
1	materials purchase (Pt/C, PtRu/C, Nafion®, gas mixtures)	training of student	training of student	purchase of PEMFC, design of test protocols
2	Prep. of Nafion® membranes	Effect of **CO**: *ads., TPD, IR*	Effect of **NH_3**: *pulse ads., IR*	Effect of **NH_3:** *consideration of protocol modifications*
3		*impact on H_2/D_2 exchange*	*impact on test reaction (HAc est.)*	Round Robin Calibration for **USFCC JHQTF**
4		*impact on H surface conc. at FC conditions (meth. dev.)*	*conductivity*	~~Effect of HCHO~~ Round Robin Calibra. for **USFCC JHQTF**
5	Prep. of Nafion® memb.	Effect of **NH_3**	Effect of **CO**	~~Effect of Ethylene~~: 400 h FC run with commercial MEA (Ion Power) (**JHQTF**)
6		Effect of **CO_2**	Effect of **Ethylene**	Effect of **CO_2**
7		Effect of **Ethylene**	Effect of **CO_2**	Effect of ~~**Ethane**~~ **THF**
8		Effect of **HCHO**	Effect of **Ethane**	Effect of **CO**: LT Study of 0.1 ppm CO (**JHQTF**)
9	**Go-No Go Decision**	**Go-No Go Decision**	**Go-No Go Decision**	**Go-No Go Decision**
	Prep. of Nafion® membs. for cond. meas.	Effect of **Ethane**	Effect of **HCHO**:	~~Effect of O_2~~: Long Term Study of low conc. of **NH_3** (**JHQTF**)
10		Effect of **HCOOH**	~~Effect of O_2~~ Effect of **Na^+, Ca^{2+}, Fe^{3+}**	~~Effect of HCOOH~~ FC **CO** studies for comparison
11		Effect of **O_2**	Effect of **HCOOH**	Effect of **Cl**: **PCE**
12		Effect of **H_2O**	Effect of **Cl**: **TCE**	Eff. of ~~**H_2O**~~ **PCE: Mass Bal.**
13		Effect of **Cl_2**: **PCE**	Effect of **H_2O**	Effect of **He, Ar, N_2**
14		Effect of **H_2S**	Effect of **He, Ar, N_2**	Effect of ~~**H_2S**~~ **Diborane**
15		Effect of **He, Ar, N_2**	~~Effect of H_2S~~ **Effect of H_2O_2 degradation**	Eff.of ~~**Impurity Mixtures**~~ **Diborane**
16	**FINAL REPORT**			

Experimental

Clemson

- **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)
  - TPD (Pt/C, 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)

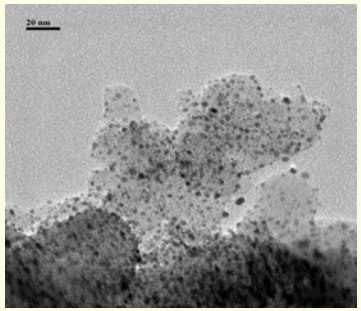
SRNL

- **Gas Impurity Mixture Generator**
  - *Kin-Tek mixture generator*
    Up to 48 mixed impurities
    Up to 500 sccm
- **FC Single Cell Test Station**
  - *Arbin FCTS 200H*
    Max. Power: 200 W
    Max. Temp.: 130°C

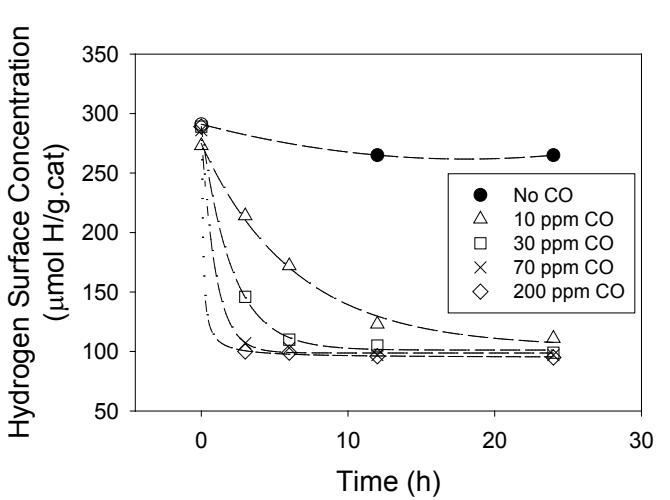
Temperatures	80° C
Pressure	1 bara (P_a=P_c)
Humidity	100 % RH anode, 50 % RH cathode
Stoichiometry (A/C)	H_2/Air = 1.2/2.0 @ 0.6 V
Pt Loading	Anode 0.1 mg Pt/cm^2 (20 wt% Pt-C)
	Cathode 0.3 mg Pt/cm^2 (40 wt% Pt-C)
Electrolyte	Nafion® 212
Cell Area	50 cm^2

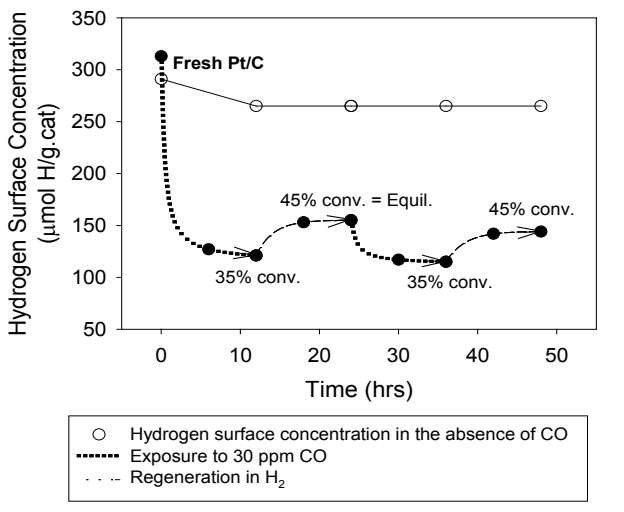
Effect of CO on H_2 Activation at 80°C on Pt/C: Absence of Water Vapor

"The effect of low concentrations of CO on H_2 adsorption and activation on Pt/C. Part 1: In the absence of humidity," ***Journal of Power Sources*** 195 (2010) 3060-3068 (Jack Z. Zhang, Zhi Ming Liu, and James G. Goodwin, Jr.).



Pt/C



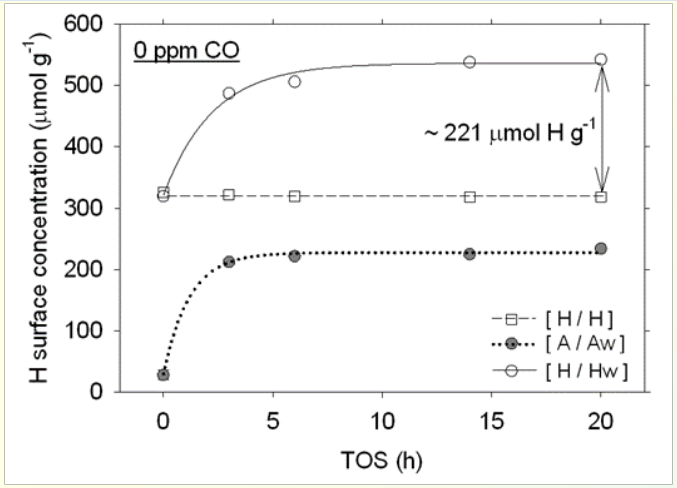


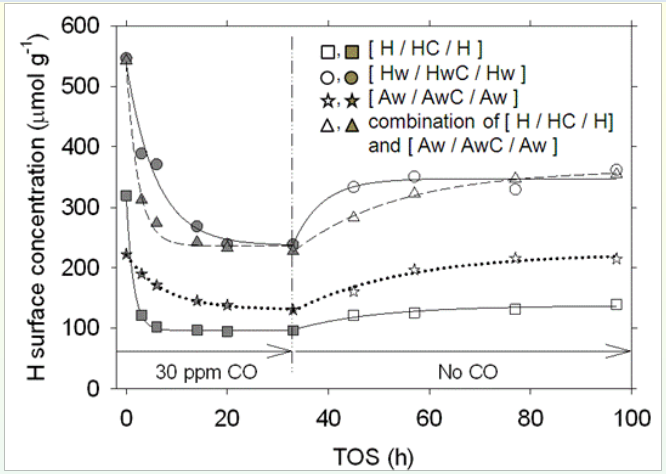
- **Presence of CO shifts the reaction away from equilibrium and increases E_a from ca. 4.5 kcal/mol (in the absence of CO) to ca. 19.3 kcal/mol (10 ppm CO) with a steady state CO surface coverage of ca. 0.44 (10 ppm).**
- **Loss of surface Pt available for H_2 activation from CO exposure is most likely due to the higher binding energy of CO on Pt vs. H.**
- **While a faster rate of poisoning is observed, further increase in CO concentration does not have a significant additional effect on both E_a and CO surface coverage.**

Contrary to electrochemical results, steady state coverage of CO on Pt is less than a ML even at 200 ppm CO. Regeneration of Pt in H_2 does not recover all poisoned Pt, but just enough where the reaction returns to being equilibrium-limited.

Effect of CO on H_2 Activation on Pt/C: Presence of Water Vapor

"The effect of low concentrations of CO on H_2 adsorption and activation on Pt/C. Part 2: In the presence of H_2O Vapor," ***submitted to Journal of Power Sources*** (Jack Z. Zhang, Kitiya Hongsirikarn, and James G. Goodwin, Jr.).





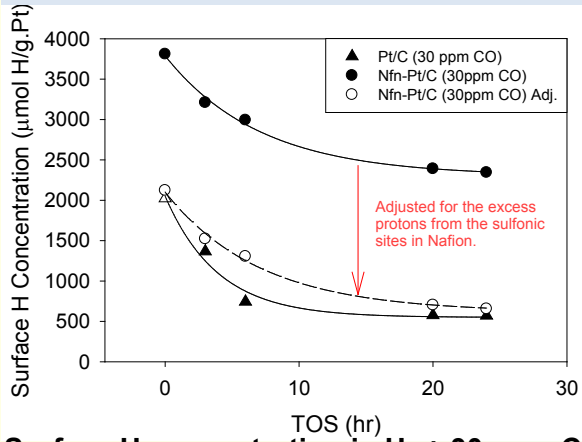
- **Total amount of strongly-adsorbed hydrogen from exposure of H_2 + H_2O [H/Hw] is the same as the sum of the exchangeable amount of hydrogen attributed to just H_2 [H/H] and just H_2O [A/Aw].**
- **This additive effect was evident regardless of presence/absence of CO, suggesting that the strong adsorption of H_2 and H_2O occurs entirely on the Pt.**
- **However, as there exists no evidence suggesting that either H_2 or H_2O cannot adsorb on specific Pt surface sites, the results are consistent with the induction of a hydrophobic Pt surface.[1]**
- **Presence of H_2O decreased rate of CO adsorption on Pt, but had very little effect on the steady state CO surface coverage [0.7 ML (no H_2O) vs. 0.66 ML (10% RH].**
- **Regeneration of poisoned Pt in H_2 + H_2O was much faster than in just H_2.**

%RH affects kinetics of adsorption/desorption but has little effect on equilibrium CO surface coverage of Pt.

(1) M.J.T.C. van der Niet, I. Dominicus, M.T.M. Koper, and L.B.F. Juurlink, Phys. Chem. Chem. Phys. 10 (2008) 7169-7179.

Effect of Nafion® on Pt/C: How is Nafion® sited?

"Interaction of Nafion® with Pt in a PEM Fuel Cell Catalyst," ***in preparation*** (Jack Z. Zhang, Kitiya Hongsirikarn, and James G. Goodwin, Jr.).



Surface H concentration in H_2 + 30 ppm CO

Sample	E_a (kcal/mol)	Rate @ 80°C (µmol HD/g.Pt-sec)
Pt/C (30 ppm CO)	20.3	1080
Nfn-Pt/C (30 ppm CO)	21.5	1065

H_2-D_2 exchange reaction: related to H_2 activation

Sample	E_a (kcal/mol)	Rate @ 30°C (µmol C_3H_8/g.Pt-sec)
Pt/C	11.6	557
Nfn-Pt/C	5.4	373

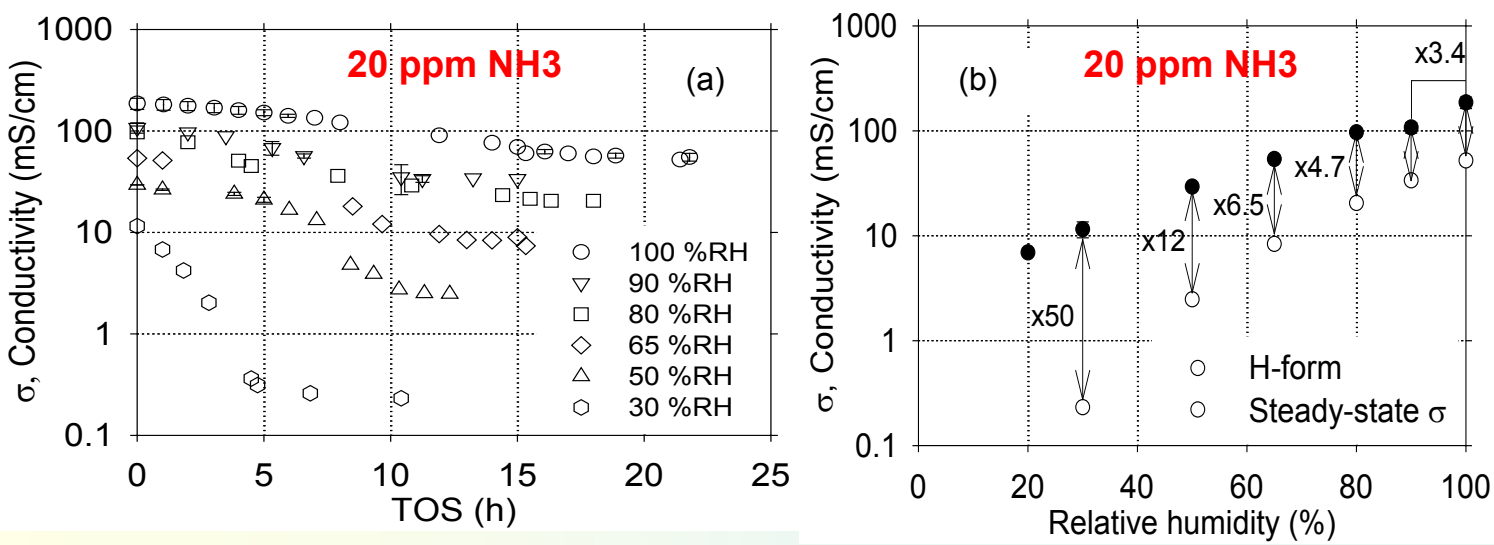
Hydrogenolysis of cyclopropane: a structure sensitive rxn. For Pt.

- **Addition of Nafion® on Pt/C significantly decreased BET SA of the catalyst, but had negligible effect on the steady-state coverage of Pt by H_2 and CO. However, kinetics of CO were slower.**
- **Similarly, presence of Nafion® did not appear to affect the rate and E_a of H_2-D_2 exchange on Pt in the presence of 30 ppm CO, suggesting the lack of blocking of Pt surface atoms by the Nafion® via either physical and/or chemical interactions.**
- **However, a clear decrease in the rate and E_a is observed when a reaction (C_3H_6 hydrogenolysis) involving a much larger molecule (C_3H_6) is employed. (Critical diameter of H_2 = 0.24 nm vs. C_3H_6 = 0.49 nm)**
- **Based on the value of E_a for C_3H_6 hydrogenolysis and <u>modeling</u> of the reaction, the decrease in rate is most likely due to diffusion limitations as a result of partial blockages of the pore mouths leading to Pt particles.**

30 wt% Nafion sits on the external surface of the C support, blocks totally small pores and partially blocks meso-macro pore openings, but does not affect H_2 or CO adsorption or H_2 activation on Pt. Pt appears to be primarily in the meso-macro pores.

Effect of Humidity on NH_3-Poisoning of the Nafion® Membrane

"Influence of Ammonia on the Conductivity of Nafion Membranes," ***Journal of Power Sources*** 195 (2010) 30-38 (Kitiya Hongsirikarn, Jack Zhang, James G.Goodwin, Jr., Scott Greenway, and Stephen Creager).



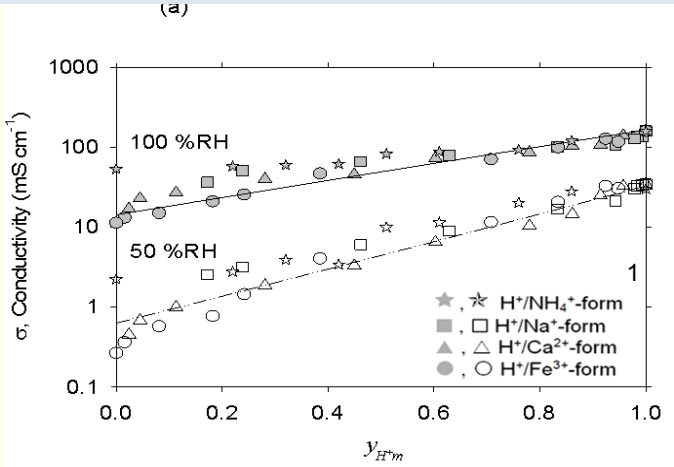
Ionic conductivity of N-211 (30-100% RH, 80°C) in the presence of 20 ppm NH_3 as a function of (a) time-on-stream (TOS); (b) relative humidity.

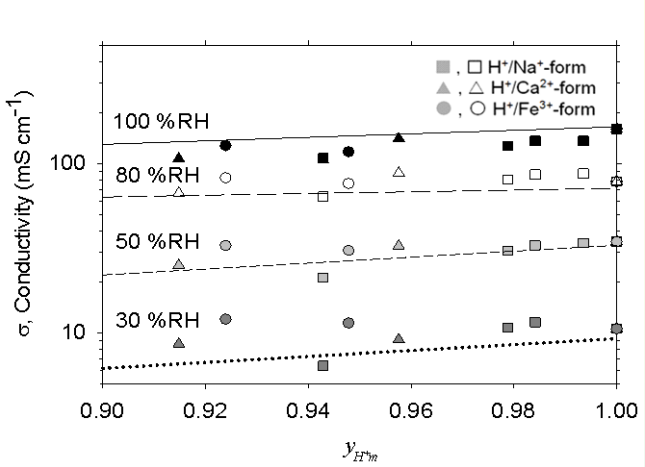
- **NH_4^+ poisons much slower at higher %RH, even for the same NH_3 conc.**
- **This slower poisoning is probably due to the competitive adsorption between H_2O and NH_3 and possibly mass transport limitations.**
- **The impact of ammonia poisoning on conductivity is more severe at low humidity than at high humidity.**

Higher impurity tolerance for NH_3 and better PEMFC performance can be expected at higher humidities.

Effect of Cations (Na^+, NH_4^+, Ca^{2+}, Fe^{3+}) on Nafion® Membrane Conductivity

"Effect of Cations (Na^+, Ca^{2+}, Fe^{3+}) on the Conductivity of a Nafion Membrane," ***Journal of Power Sources*** 195 (2010) 7213-7220 (Kitiya Hongsirikarn, James G. Goodwin, Jr., Scott Greenway, and Stephen Creager).





Conductivity of cationic-contaminated N-211 membranes at 80°C .

$y_{H+m} + y_{Mn+m} = 1$ (y_{H+m} and y_{Mn+m} are the fractions of sulfonic sites having protons and other cations neutralizing site, respectively, in the membrane).

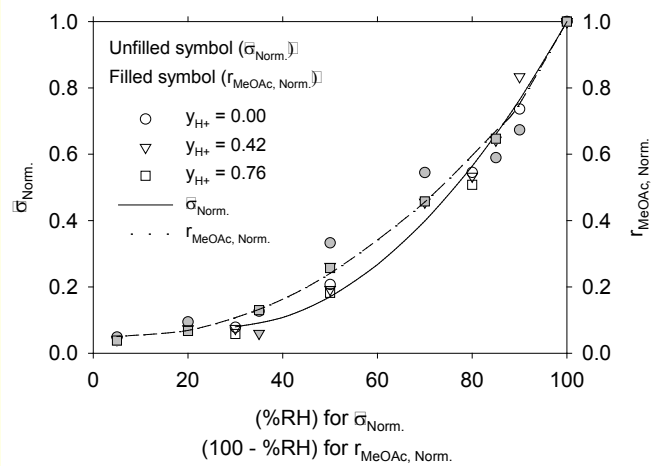
- **At the same y_{H+m}, the conductivities of membranes poisoned with monovalent cations (i.e., Na^+, NH_4^+) were similar, but slightly higher than those with higher valent cations (Ca^{2+}, Fe^{3+}).**
- **The effect of cations on the conductivity of a membrane having trace amounts of cations was minimal and was proportional to y_{H+m}.**
- **In practical fuel cell operations, the effect of NH_4^+ ions on PEMFC performance should be less than that of non-proton cations because of the ability of NH_4^+ to act as a proton carrier and the possibility of NH_3 removal at the cathode.**

Metal cations poison Nafion® in a similar way as NH_3 with the severity related to their charge. However, they are harder to remove in situ.

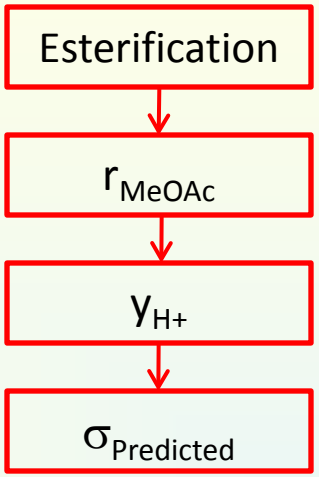
(1) K. Hongsirikarn et al., J. Power sources (1) (2010) 30

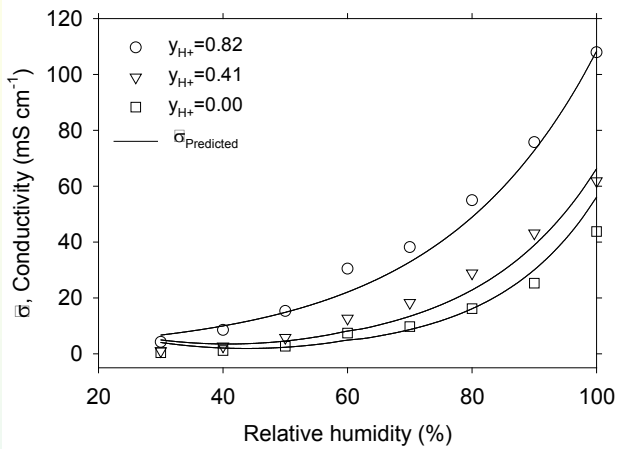
Prediction of Conductivity of a Cationic-Contaminated Membrane

"Esterification as a Diagnostic Tool to Predict Proton Conductivity Affected by Impurities on Nafion Components for Proton Exchange Membrane Fuel Cells," ***Journal of Power Sources*** 195 (2010) 3416-3424 (Kitiya Hongsirikarn, Xunhua Mo, and James G. Goodwin, Jr.).



Comparison of the $\sigma_{Norm.}$ and $r_{MeOAc, Norm.}$ of N-211 poisoned with NH_3 at 80°C.





Experimental and predicted σ of N-211 in the H^+/Na^+-form at 80°C.

$$\text{Normalized } \sigma(\sigma_{Norm.}) = \frac{(\sigma_{y_{H^+}=1} - \sigma_{y_{H^+}})_{RH,80\,°C}}{(\sigma_{y_{H^+}=1} - \sigma_{y_{H^+}})_{100\%\ RH,80\,°C}}$$

$$\text{Normalized } r_{MeOAc}(r_{MeOAc,Norm.}) = \frac{(r_{MeOAc,y_{H^+}=1} - r_{MeOAc,y_{H^+}})_{RH,80\,°C}}{(r_{MeOAc,y_{H^+}=1} - r_{MeOAc,y_{H^+}})_{0\%\ RH,80\,°C}}$$

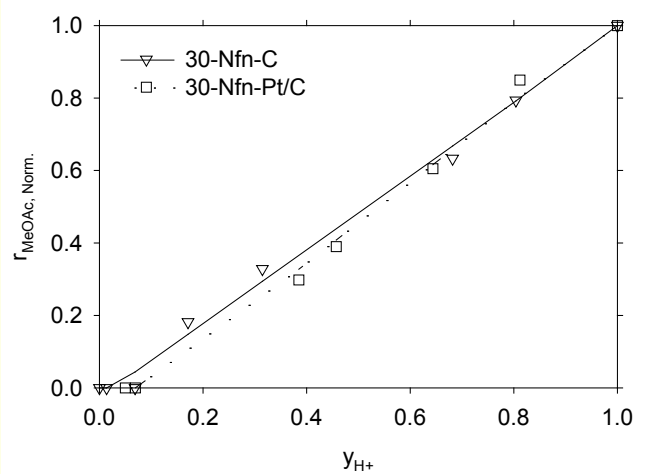
$$\left[(\sigma_{yH+})_{\%RH,80°C}\right]_{Na^+} \approx \left[(\sigma_{yH+=1})_{\%RH,80°C}\right] - \sigma_{Norm.,Predicted}\left[(\sigma_{yH+=1} - \sigma_{yH+})_{100\%RH,80°C}\right]_{NH_4^+}$$

- **Experimental results for detrimental effect of NH_3 on conductivity (σ) and acetic acid esterification with MeOH (rate, r_{MeOAc}) for a Nafion membrane were used to develop the methodology & correlation.**
- **$r_{MeOAc, Norm.}$ correlates excellently with $\sigma_{Norm.}$ at fuel cell conditions for Na^+ poisoning.**

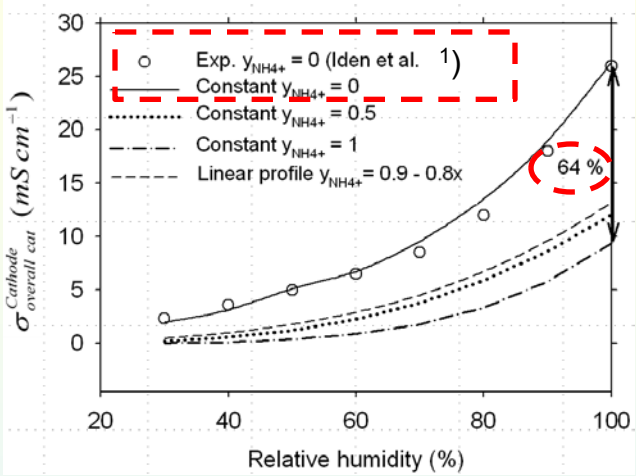
The proton conductivity of a Nafion® membrane exposed to a poison/impurity can be accurately predicted using a Bronsted acid catalyzed reaction whose rate is determined by proton concentration. This could especially be useful to study poisoning in a catalyst layer.

Prediction of Effective Conductivity of Nafion® in the Catalyst Layer

"Prediction of the Effective Conductivity of Nafion in the Catalyst Layer of a PEMFC," ***Journal of Power Sources* 195** (2010) 5493-5500 (Kitiya Hongsirikarn, Xunhua Mo, Zhiming Liu, and James G. Goodwin, Jr.).



$r_{MeOAc, Norm.}$ of Nafion® supported materials at 50 %RH and 80°C.



Prediction for an NH_4^+-contaminated cathode catalyst layer at 80°C.

Esterification → y_{H+} → an agglomerate model[2] → $\sigma_{Predicted}$

Esterification can be used to predict conductivity of Nafion® in the catalyst layer.

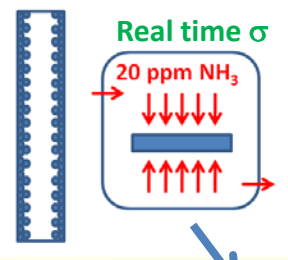
- **$r_{MeOAc, Norm.}$ of Nafion® in cat. layer has equiv. relationship with y_{H+} as Nafion® memb.**
- **Thus, esterification can be used to determine eff. of impurities on y_{H+} in cat. layer.**
- **The predicted values agree well with the limited available experimental data.[1]**
- **Predicted $\sigma_{overall\ cat.}$ for the fully NH_4^+-form was 64% lower than that of the H^+-form, similar to performance loss in a PEMFC (49-77%)[3] under equivalent conditions.**

(1) H. Iden et al., J. Electrochem. Soc. 156 (9) (2009) B1078
(2) F. Jaouen et al., J. Electrochem. Soc. 149 (4) (2002) A437
(3) Uribe et al., J. Electrochem. Soc. 149 (3) (2002) A293

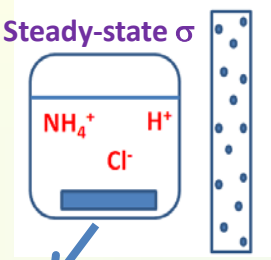
Effect of NH_4^+ Distribution on Nafion® Conductivity

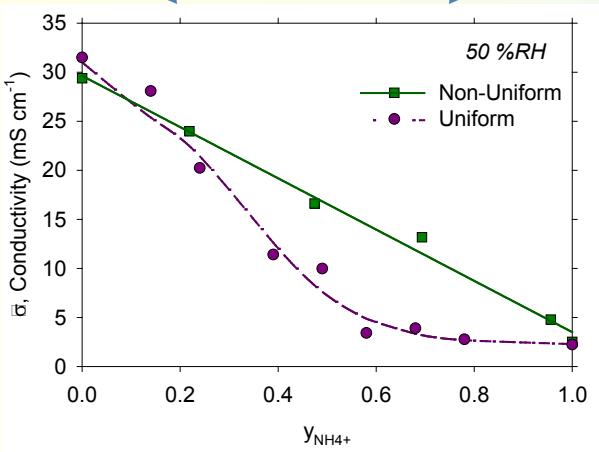
"Effect of Ammonium Ion Distribution on Nafion® Conductivity," ***Journal of Power Sources*** 196 (2011) 644-651(Kitiya Hongsirikarn, Thirapong Napapruekchart, Xunhua Mo, and James G. Goodwin, Jr.)

Non-Uniform NH_3 poisoning



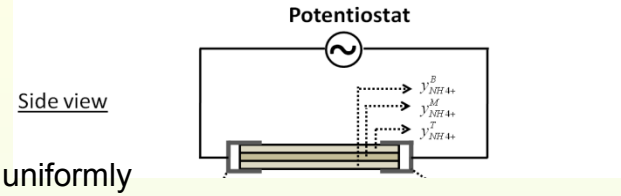
Uniform NH_4^+ poisoning



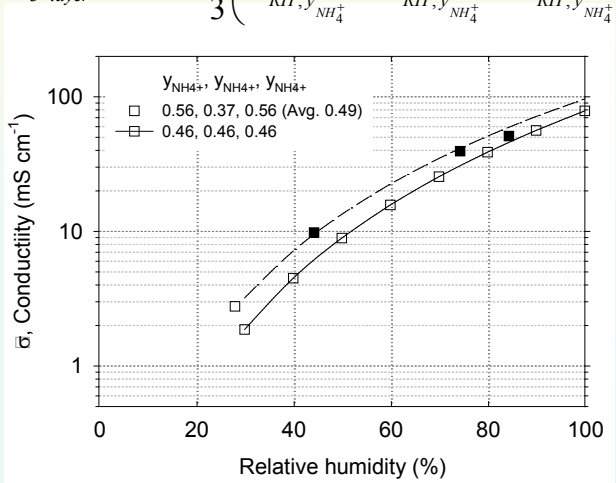


- σ in a Nafion® membrane is affected not only by y_{NH4+} but also by its distribution.

Sandwich of 3 uniformly poisoned membranes



$$\sigma_{3-layer} = \frac{1}{3}\left(\sigma_{RH,y^T_{NH_4^+}} + \sigma_{RH,y^M_{NH_4^+}} + \sigma_{RH,y^B_{NH_4^+}}\right)$$



- **Inclusion of terms for non-homogeneity of impurity distribution in a membrane should improve prediction of fuel cell performance.**

$$\sigma_{overall,mem} = \int_{x_H}^{x_L} \sigma_{RH,y_{NH_4^+}} \, dx$$

During poisoning of a membrane, distribution of the poison can affect H conductivity of the membrane.

Effect of H_2O_2 on Nafion® Properties and Conductivity

"Effect of H_2O_2 on Nafion® Properties and Conductivity at Fuel Cell Conditions," **Journal of Power Sources** 196 (2011) 3060-3072 (Kitiya Hongsirikarn, Xunhua Mo, James G. Goodwin, Jr., and Stephen Creager).

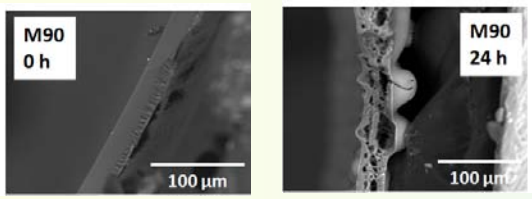
- **Even if a fuel cell is operated in neat H_2 and oxidant streams, degradation of its performance can occur due to:**
  - **Decrease in active surface area of the Pt catalyst**
  - **Decomposition of Nafion®**
- **Membrane degraded due to radical attack (OH•, OOH•) and material corrosion (Fe^{2+}, Fe^{3+}) during fuel cell operation.**

$$Nafion-Fe^{2+} + H_2O_2 \longrightarrow Nafion-Fe^{3+} + OH\bullet + OH^-$$

$$H_2O_2 + OH\bullet \longrightarrow OOH\bullet + H_2O$$

$$Nafion-Fe^{3+} + OH^- \xrightarrow{h\nu} Nafion-Fe^{2+} + OH\bullet$$

M90: Nafion® with 10% of H^+ replaced with Fe^{2+}



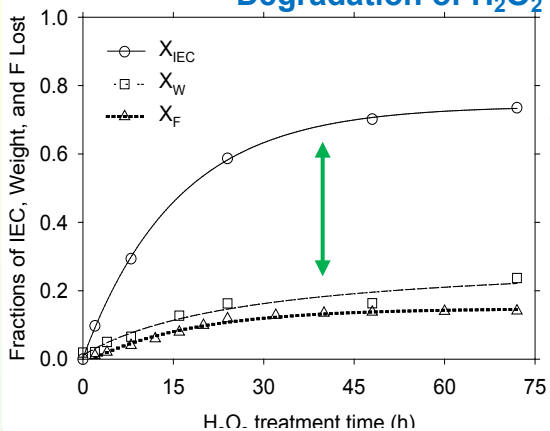
- **The level of Nafion® degradation defined as follows:**

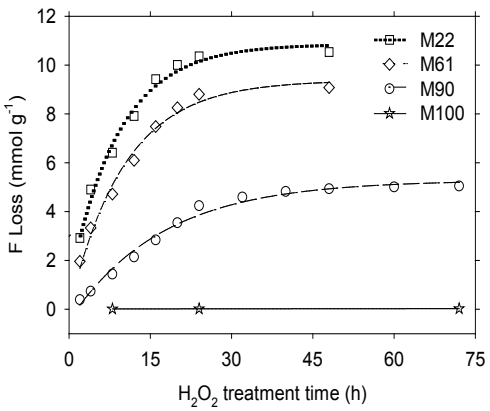
$$IEC\ fraction\ loss: X_{IEC} = \frac{y^0_{H^+-Fe} - y^t_{H^+-Fe}}{y^0_{H^+-Fe}}$$

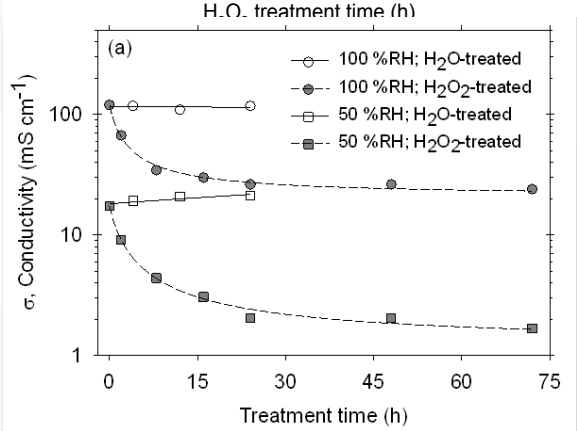
$$Weight\ loss\ fraction: X_W = \frac{W_0 - W_t}{W_0}$$

$$Fluorine\ loss\ fraction: X_F = \frac{[C_F]_t V_{H_2O_2}}{W_0 F_0}$$

Degradation of H_2O_2-treated M90 membranes





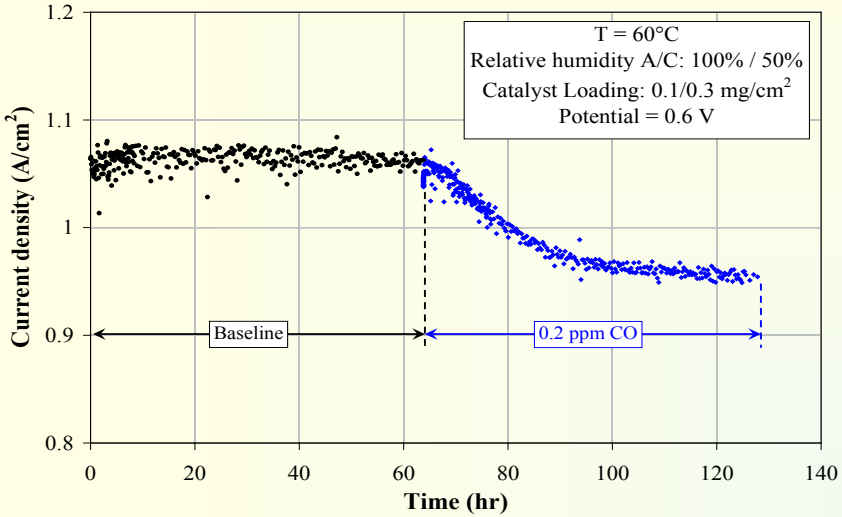


- **The values of X_{IEC} are higher than those of X_W and X_F. Reactive radicals not only cause the cleavage of Nafion's matrix, but may also cause the formation of cross-linking S-O-S.**

- **Reactive radicals rapidly decompose a Nafion membrane, significantly decreasing conductivity (4.6-20 times depending on humidity and degradation level), and eventually degrade PEMFC performance.**

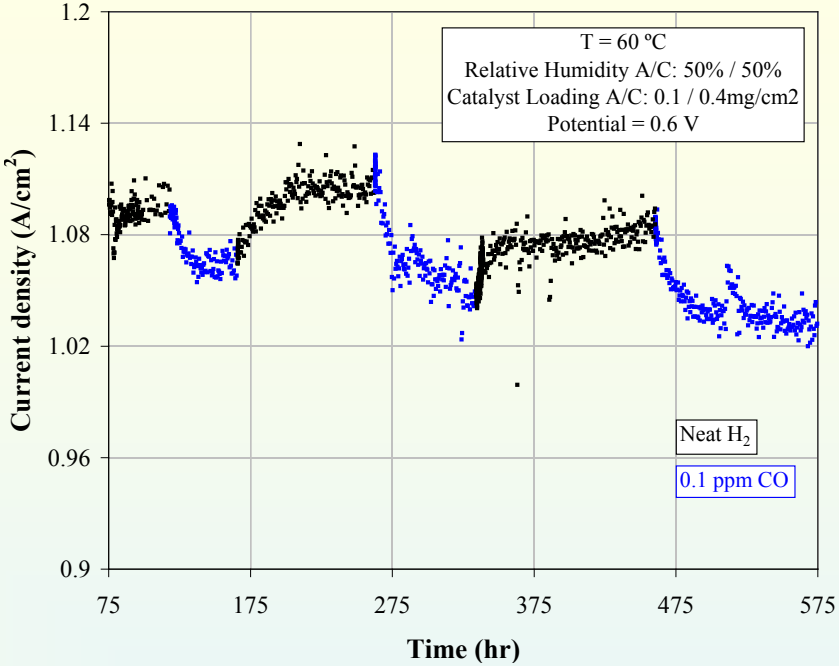
The membrane deterioration rate due to H_2O_2 is significantly influenced by Fe composition in the membrane and H_2O_2 exposure time. Membrane conductivity is heavily impacted.

Effects of 0.2 and 0.1 ppm CO on Fuel Cell Performance



Ion Power MEA and 0.2 ppm CO (Corrected for MEA Baseline)

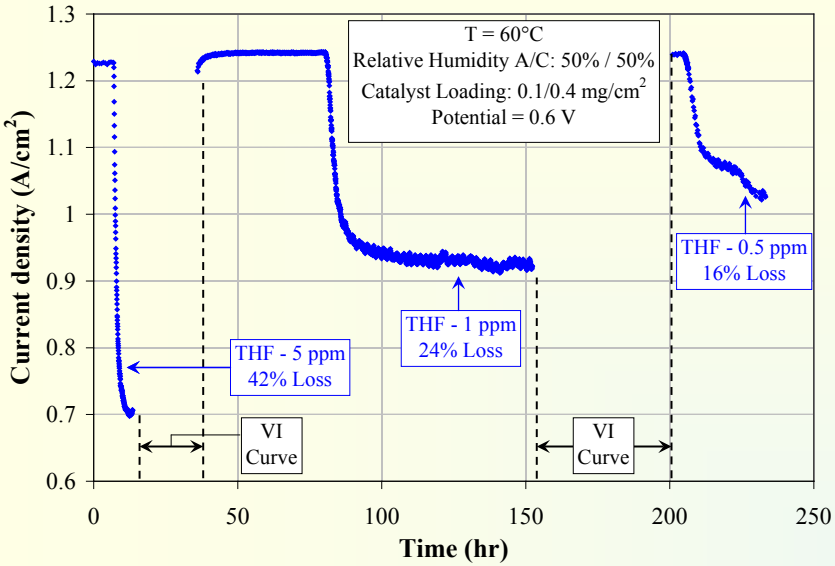
- **~8% of performance is lost in 30 hours after cell is exposed to 0.2 ppm of CO.**
- **Complete recovery is observed after CV.**



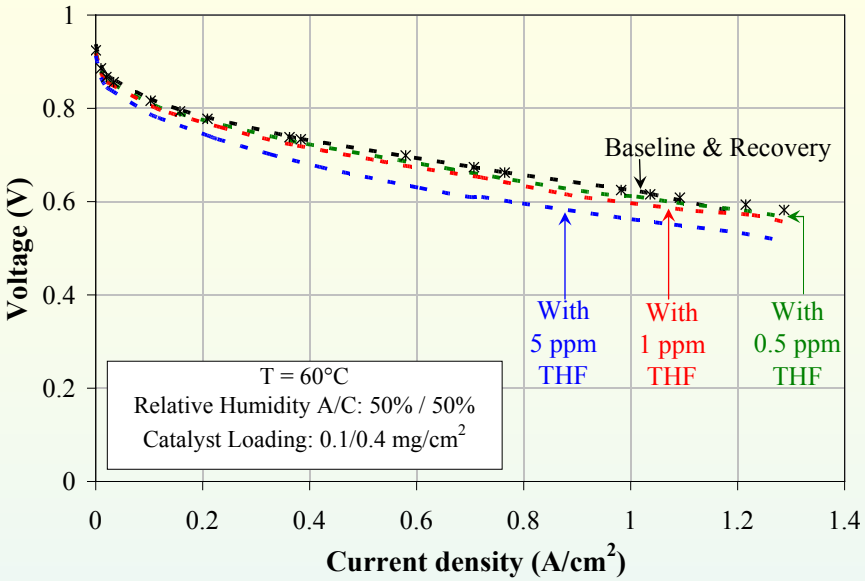
- **3% - 4% of performance is lost in periods between 20-40 hours after cell is exposed to 0.1 ppm of CO.**
- **Complete recovery is observed after CO is stopped.**

These results indicate for the first time that the degradation effects of CO at sub-ppm levels are enhanced when the FC is operated at voltage controlled.

Effects of THF on FC Performance



Poisoning with THF and Recovery

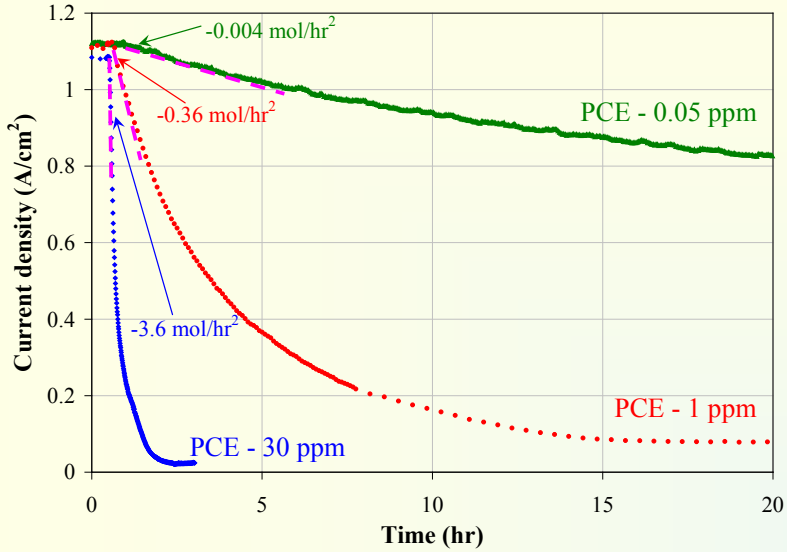


Cell Performance

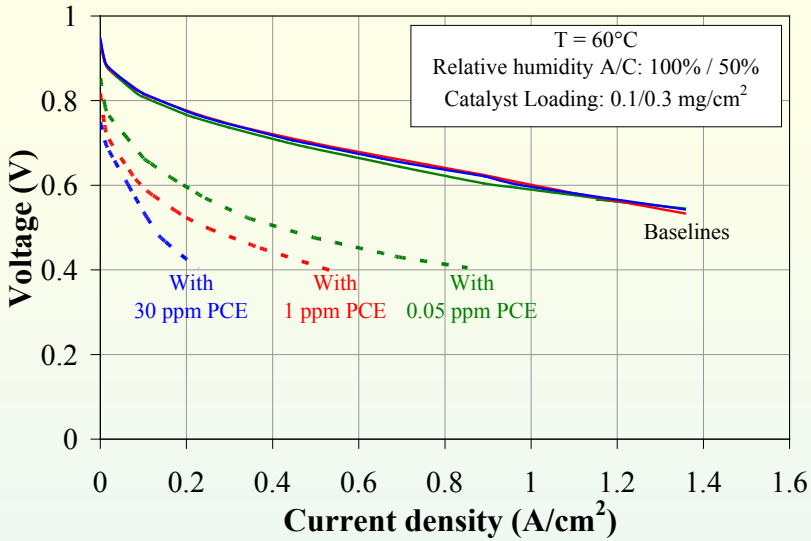
- **Tetrahydrofuran (C_4H_8O, THF) has been used to characterize the performance effects that heterocyclic compounds can have on fuel cell performance.**
  - **THF is a popular solvent used in many chemical synthesis which include hydrogen storage materials.**
- **Approximately 40% loss in performance is observed.**
- **Full recovery is observed as soon as THF is removed from the fuel stream.**

THF affects the FC performance, however full recovery is observed after the impurity is removed from the H_2 stream.

PCE Cell Poisoning at 0.6 V



Poisoning with PCE at 0.6 V

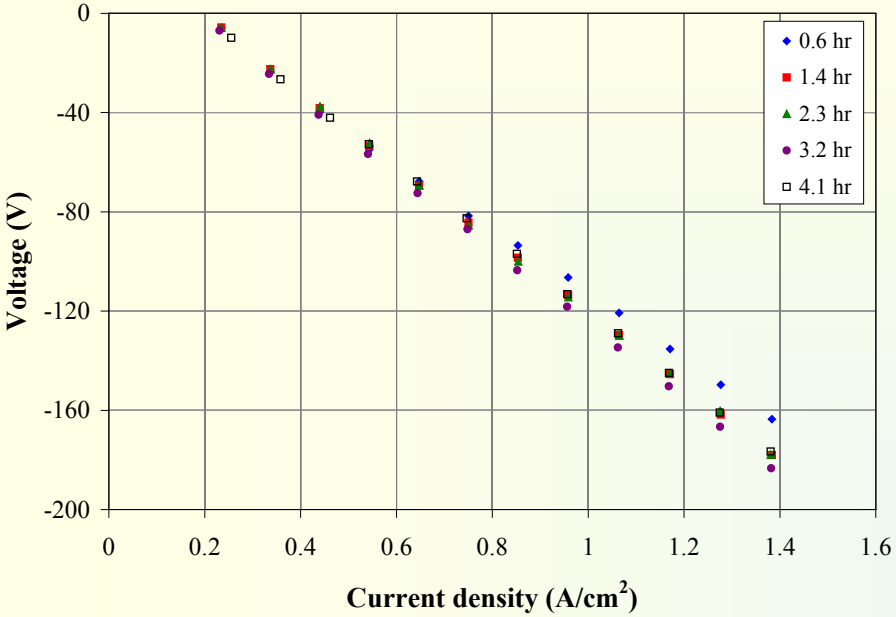


Cell Performance after steady state poisoning

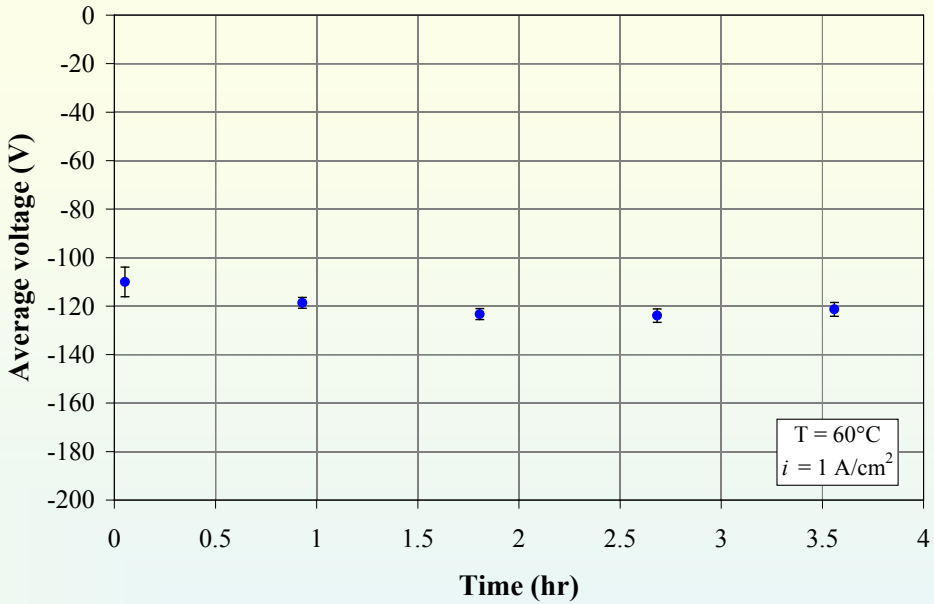
- **Perchloroethylene (C_2Cl_4, PCE) has been used to characterize the performance effects that chlorinated cleaning agents (house keeping compounds) can have on fuel cell performance.**
  - **PCE is a chlorinated cleaning agent that can be used during "house keeping" that could be present in the fuel delivery system.**
- **Even at 50 ppb the effects are significant.**

PCE tends to completely poison the cell, even at 50 ppb.

H_2 Pump Experiment with 30 ppm PCE Poisoning



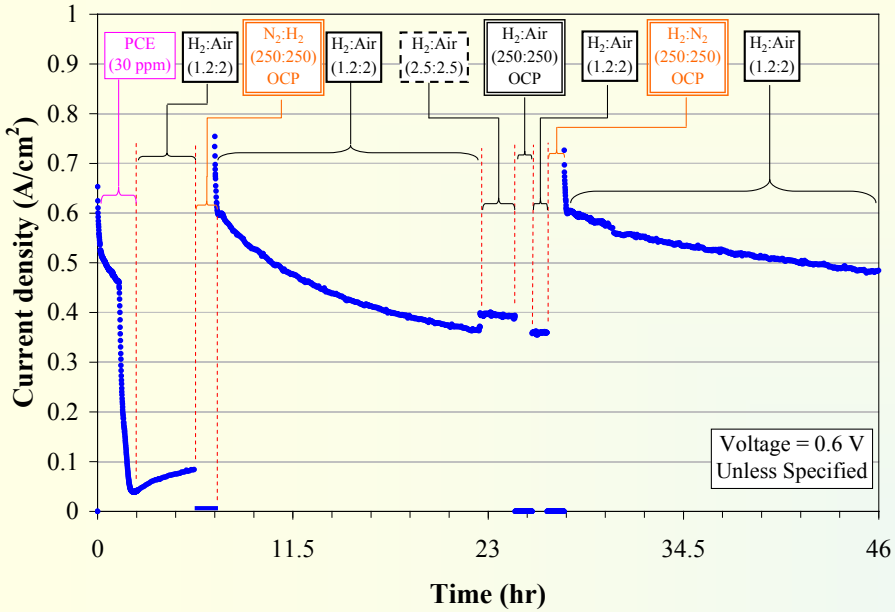
Polarization H_2 pump section



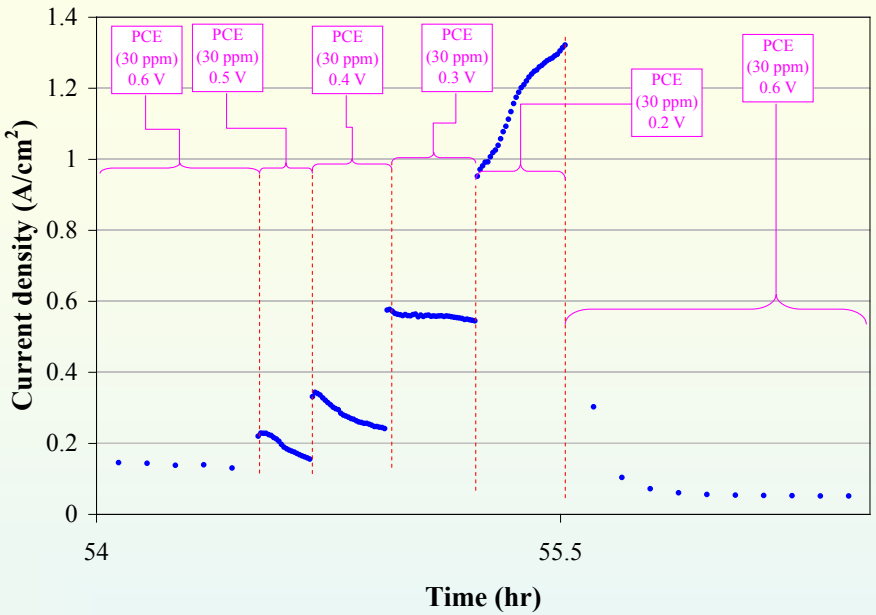
Overpotential at 50 A (1 A/cm^2) H_2 pump

No effects on the overpotential are observed in the hydrogen redox reaction or membrane resistance even with 30 ppm PCE exposure.

PCE Performance Recovery Studies



Recovery under different operating conditions

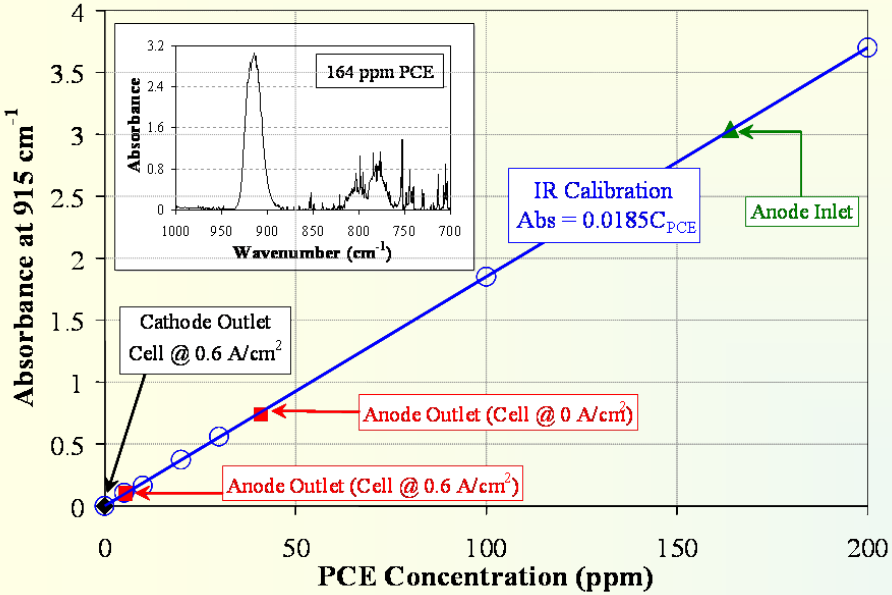


Cell Performance under different operating voltages

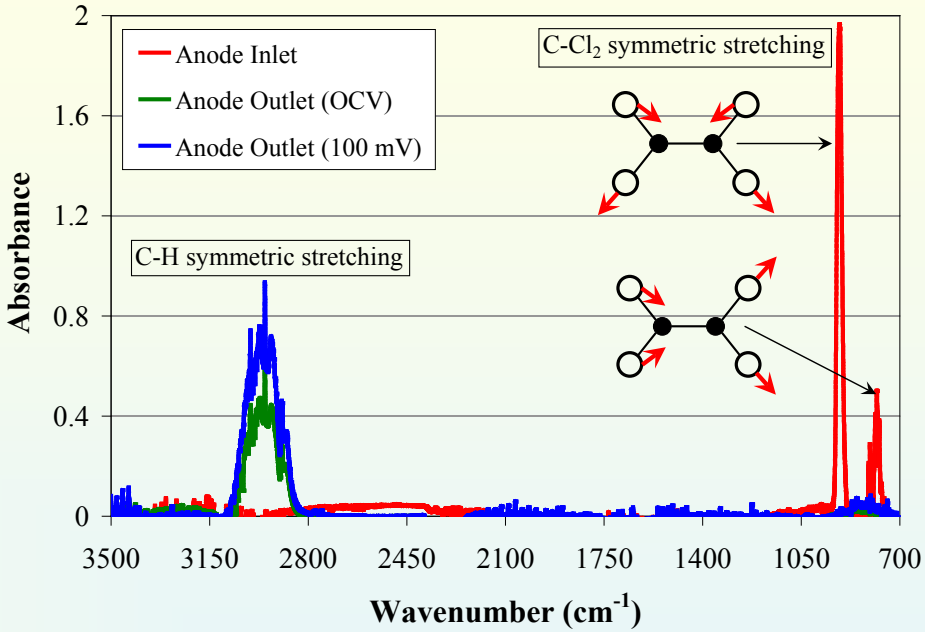
- **Best recovery was when N_2:H_2 was used for Anode:Cathode during OCP.**
- **No effect was observed with increasing of gas flow during normal operation.**
- **PCE shows no effect on performance when cell uses H_2:Air at low voltages.**
- **Complete recovery is observed after extended shutdown with N_2 purge.**

PCE effects are minimized and reversed by either imposing or changing the operating conditions so that the FC operates at low potentials.

PCE Mass Balance Studies



IR studies



Decomposition Products of the PCE

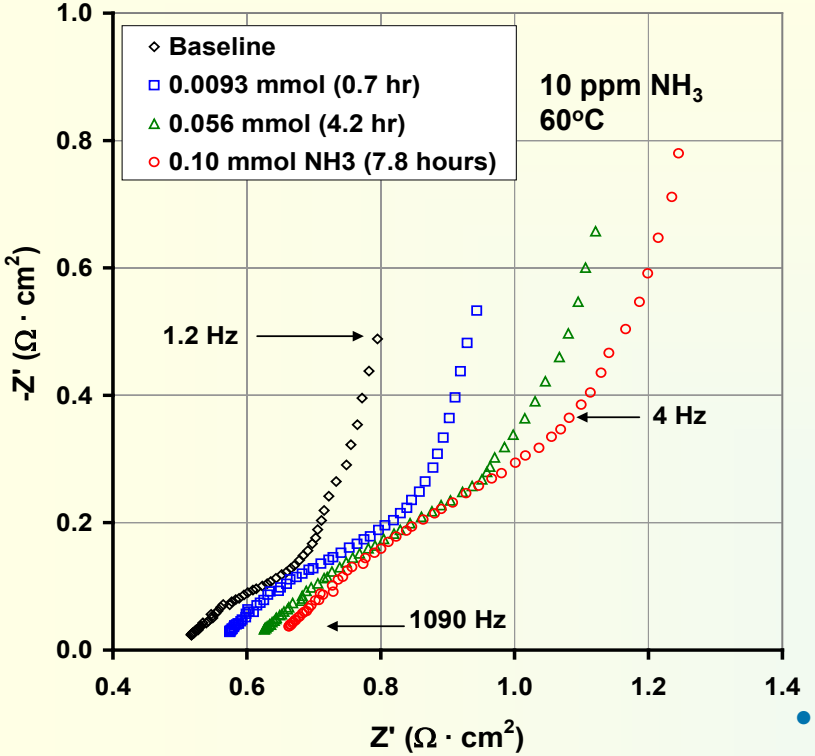
- **IR data shows PCE immediately reacts catalytically with the catalyst layer.**
- **Same decomposition products are observed during H_2 pump experiments as well as FC.**
- **Effects observed on FC performance must be associated to the decomposition products.**

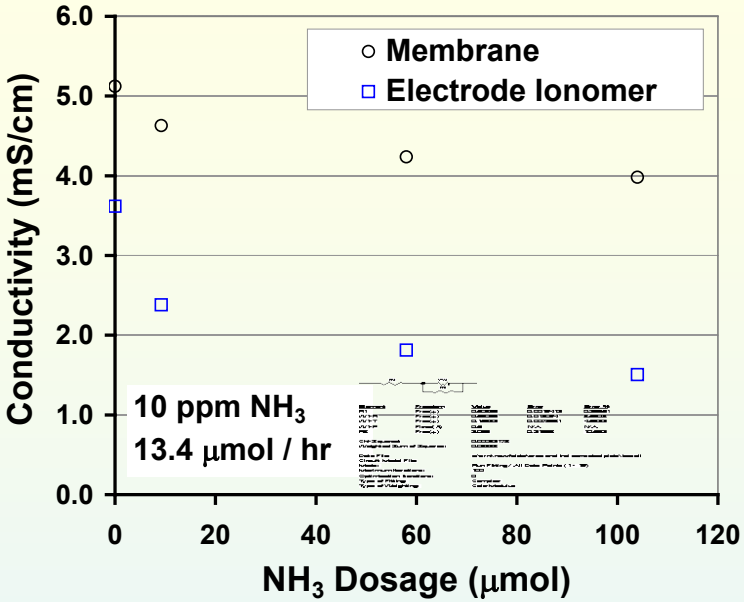
PCE reacts at the anode and is likely the decomposition products are poisoning the cathode electrode.

O. Bertrand et al, J. Phys. Chem. B, 109, 13312-13321 (2005)

W. Den et al., Chem. Eng. Sci., 61, 7909 – 7923 (2006)

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



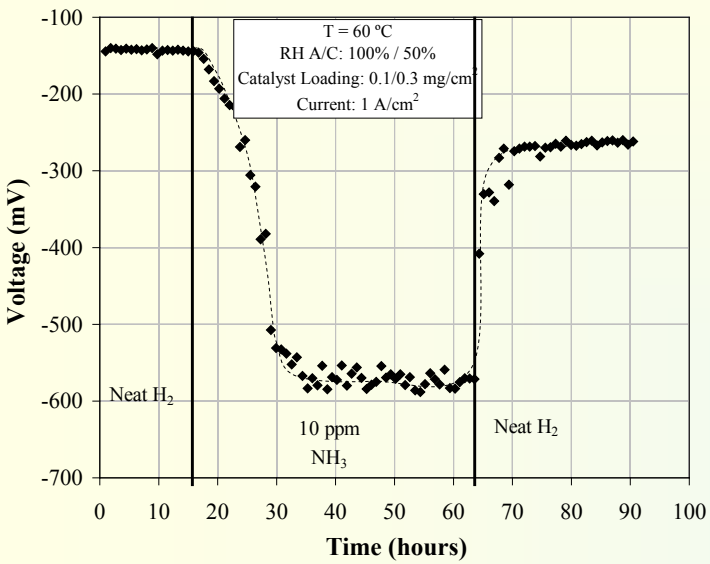


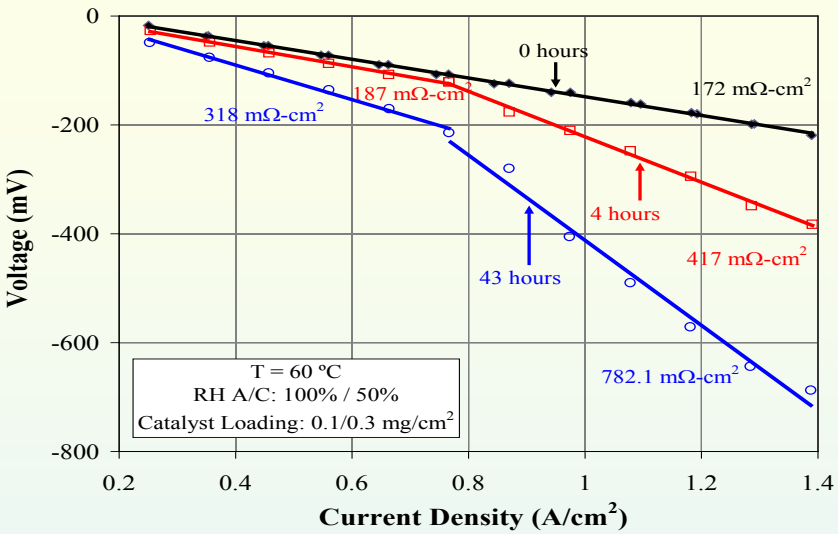
- Ion Power MEA (0.3/0.3 mg Pt)
- Working Electrode: 10 ppm NH3 in Ar at 500 sccm (13.4 µmol / hr); 75% RH
- Ref. / Counter Electrode: H2 at 500 sccm ; 75% RH
- Potential Bias (11 mV vs. OCV)
- Perturbation (10 mV)
- Inductance Correction (0.36 mH)

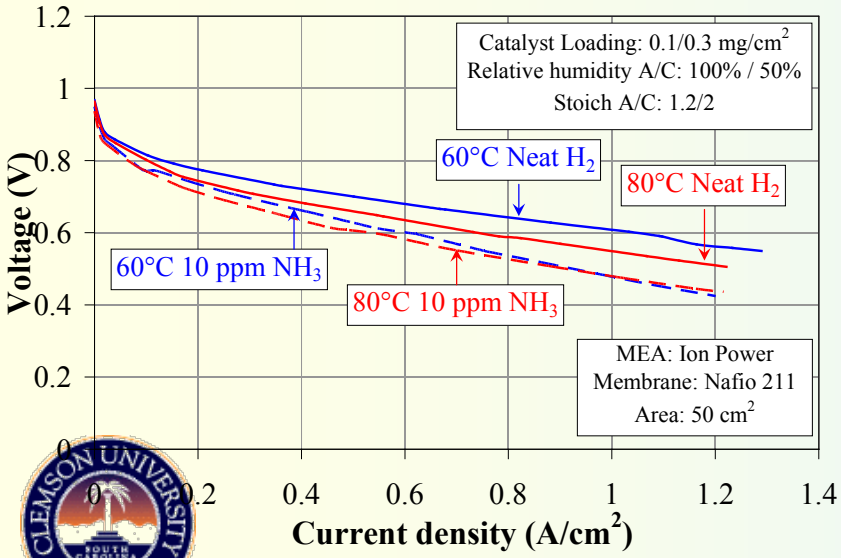
- The baseline run before poisoning is shown in black.
- Area corrected membrane resistance is given by the high frequency intercept with the x-axis.
- The ionomer resistance is proportional to the length of the "45°" line segment between 1090 Hz and ca. 4 Hz.

This analysis method shows that both the membrane and electrode ionomer resistances increase during NH_3 poisoning.

Effects of NH_3 at 10 ppm on Membrane & Ionomer @ 60ºC during H_2 Pump experiments



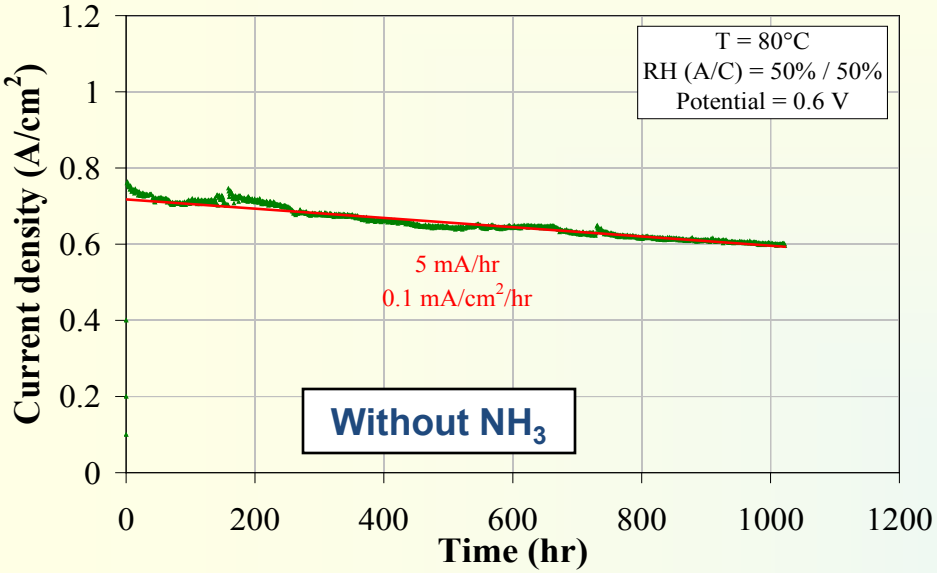


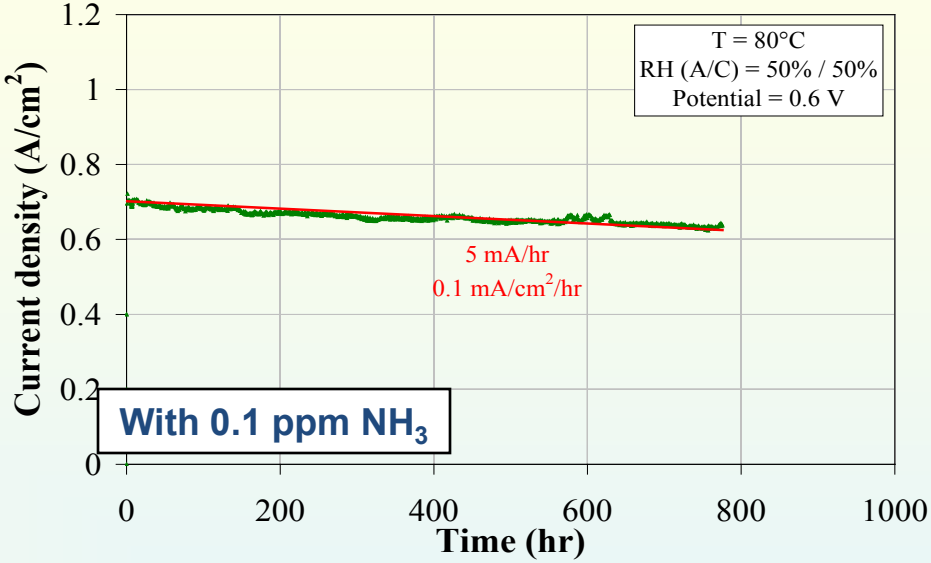


- At 10 ppm NH_3 causes major degradation on the anode performance.
  - Close to 500 mV of overpotential
- Complete recovery is never attained after 25 hrs of flowing neat hydrogen.
- Degradation seems to be higher during the H2 pump experiments.

Using H_2 pump one can assess the impurity effect on the ionomer and membrane.

Effects of NH_3 at the Maximum ISO Specified Level





Effect of 0.1 ppm NH_3 on Gore MEA @ 80 C

- **At 0.1 ppm, NH_3 does not affect baselines of Gore and Ion Power MEAs.**

No measurable effects on performance can be observed when flowing NH_3 at ISO concentrations

Overview of Impurity Effects

Impurity	Effect on FC Performance	Component Studies[a]			
		Max. Conc. Tested	Max.P_i (atm)	Effect on H_2 activation and surface hydrogen conc. on Pt/C[b]	Effect on Nafion conductivity [c]
Inerts (N_2, Ar, He)	No	50 – 80%	1.0 – 1.6	No	No
CO_2	TBD	500 ppm	0.0005	TBD	No
CO	Major	2-50 ppm	to 0.00005	Major	No
NH_3	Major	10-5000 ppm	to 0.005	Minimal	Major
Formic acid	TBD	400 ppm	0.0004	TBD	No
Ethylene	TBD	400 ppm	0.0004	In progress	No
Acetaldehyde	TBD	250 ppm	0.00025	TBD	No
Perchloroethylene	Major	30-400 ppm	0.0004	In progress	No
Tetrahydrofuran (THF)	Yes –but reversible	400 ppm	0.0004	TBD	No
Propane (C_3H_8)	No	100 ppm	0.0001	Minimal	No
Butane (C_4H_{10})	No	100 ppm	0.0001	Minimal	No
Pentane (C_5H_{12})	No	100 ppm	0.0001	Minimal	No
Hexane (C_6H_{14})	No	100 ppm	0.0001	Minimal	No
Heptane (C_7H_{16})	No	100 ppm	0.0001	Minimal	No
Cations (Na^+, Ca^{2+}, Fe^{3+})	Major [Ref. (1)-(3)]	NA	NA	Minimal	Major

[a] At 80°C.
[b] Impurities were exposed to Pt/C catalyst over a 24 h period.
[c] Impurities were exposed to a Nafion membrane over a 12 h period.

(1) B. S. Pivovar et al., *Handbook of Fuel Cells*. (Wiley, 2009)
(2) B. L. Kienitz et al., Electrochim. Acta 54 (2009) 1671
(3) T. A. Greszler et al., *Handbook of Fuel Cells*. (Wiley, 2009)

Preliminary Mitigation Strategies

To date, the following preliminary impurity mitigation strategies can be proposed based on the findings of this project:

- **Use of higher %RH results in a smaller decrease in conductivity with NH_3 poisoning. Thus, a higher %RH is recommended for FC operation to increase the performance and lifetime when trace amounts of NH_3 are present in the fuel.**
- **Fuel cells can tolerate up to 0.1 ppm of NH_3 (maximum ISO specified level) for long periods of time.**
- **NH_3 poisoning can be partially reversed with time, however the impact of metal cations while similar, leads to an MEA that is essentially permanently degraded.**
- **Although water vapor does not appear to strongly affect CO poisoning at equilibrium, it does appear to increase the kinetics of recovery of the Pt surface in hydrogen. Thus, use of higher humidity during regeneration after exposure to CO is suggested.**
- **Chlorine-containing impurities like PCE can be detrimental to FC performance at even ppb levels. Their effect can probably be minimized and reversed by either imposing or changing the operating conditions so that the FC operates at low potentials.**

Obviously, the actual materials and operational conditions chosen for use in a FC must be determined by an optimization of material properties, operation conditions, possible mitigation strategies to minimize the effect of impurities, and desired FC performance.

Collaborations

Researchers at Clemson and SRNL are in contact on a bi-weekly basis by phone and e-mail and hold joint meetings ca. every month for discussion of results and for planning purposes. There is also collaboration on scientific papers.

Clemson University

Prime, within DOE H_2 Prog.

- ***Ex-situ*** **characterization of Pt/C, Nafion-Pt/C, and Nafion membrane.**
- **Investigation of effect of poisoning of the Pt catalyst on H_2 activation using H_2-D_2 exchange and measurement of H surface coverage of Pt and catalyst support.**
- **Investigation of poisoning of the ionomer on the catalyst and in the membrane using conductivity measurements and a characteristic BA catalyzed reaction.**

Savannah River National Lab

Sub, within DOE H_2 Prog.

- **Determination of fuel cell performance.**
- ***In-situ*** **poisoning mechanism studies on MEAs.**
- **Contaminant testing down to ISO fuel quality standard.**
- **CV measurements of contaminant adsorption on catalyst surface.**
- **Understanding electrochemical surface cleaning methods.**

John Deere

Cost-Share Partner, Industry

Advice on FC operation and contaminants.

Work at Clemson and SRNL underway to provide fundamental measurements for use in FC modeling efforts.

Modeling results will be useful in better understanding impact of impurity mechanism on FC performance.

Modeling Group at ANL

Proposed Future Work (2011)

- **Activities**
  - Complete the studies of the effect of perchloroethylene (PCE) on H_2 activation on Pt/C to understand poisoning mechanisms and rates. Compare results to those for fuel cell tests with PCE at SRNL.
  - Complete CO poisoning studies at SRNL using PEM fuel cell and compare with Pt/C results for H_2/D_2 exchange and H surface concentration at Clemson.
  - Work with DOE H_2 Fuel Quality Working Group to Support ISO Standard Process.
  - Provide Argonne Nat. Lab Modeling Group with phenomenological data on NH_3 poisoning of Nafion and CO and PCE poisoning of Pt.
  - Develop strategies for mitigating the effects of FC poisons.

- **Upcoming Milestones**
  - Write final report.

- **Decision Points** None

Summary

- *The effects of CO_2, C_2-C_7 paraffins, HCOOH and N_2 on Nafion® conductivity or Pt for H_2 activation were insignificant.*
- *PEM fuel cell studies on the effects of 18 PPM THF found ~ 40% loss in performance and full recovery once THF was removed from the fuel stream.*
- *Perchloroethylene (PCE) indicate that PCE affects the cell mostly at high potentials.*
- *PEM fuel cell studies on the effects of 18 PPM THF found ~ 40% loss in performance and full recovery once THF was removed from the fuel stream.*
- *Investigation of the long-term NH_3 poisoning with NH_3 at 0.1 ppm found no appreciable degradation at 60°C and 80°C with the introduction of NH_3 at the maximum ISO specified level.*
- *CO poisoning experiments performed in PEM fuel cell tests at SRNL correlate well with the results from CO poisoning experiments of H_2 activation on Nfn-Pt/C at Clemson.*
- **Contrary to electrochemical results, steady state coverage of CO on Pt is less than 1 ML, even at 200 ppm CO, and regeneration of Pt in H_2 does not recover all poisoned Pt, but just enough where the reaction returns to being equilibrium-limited.**
- **%RH affects kinetics of adsorption/desorption but has little effect on equilibrium CO surface coverage of Pt.**

Summary (cont.)

- 30 wt% Nafion® sits on the external surface of the C support, blocks totally small pores and partially blocks meso-macro pore openings, but does not affect H_2 or CO adsorption or H_2 activation on Pt. Pt appears to be primarily in the meso-macro pores.
- Higher impurity tolerance for NH_3 and better PEMFC performance can be expected at higher humidities.
- Metal cations poison Nafion® in a similar way as NH_3 with the severity related to their charge. However, they are harder to remove in situ.
- The proton conductivity of a Nafion® membrane exposed to a poison/impurity can be accurately predicted using a simple Bronsted acid catalyzed reaction like esterification whose rate is determined by proton concentration. This could especially be useful to study poisoning in a catalyst layer.
- *Esterification can be used to predict conductivity of Nafion® in the catalyst layer.*
- During poisoning of a membrane, distribution of the poison can affect H conductivity of the membrane.
- The membrane deterioration rate due to H_2O_2 is significantly influenced by Fe composition in the membrane and H_2O_2 exposure time. Membrane conductivity is heavily impacted.

Technical Back-Up Slides

H_2/D_2 Exchange Mechanism

- **H_2/D_2 exchange [300 < T (K) < 500]**
  - **Bonhoeffer-Farkas mechanism***
    (S denotes an active catalyst site)
  - **The adsorption-dissociation step is referred to as the Tafel reaction**

$$H_2 + D_2 + 2S \leftrightarrow 2HS + 2DS$$
$$2HS + 2DS \leftrightarrow 2SHDS$$
$$2SHDS \leftrightarrow 2HD + 4S$$

- **In the temperature region indicated**
  - **Rate of surface diffusion is very rapid**
  - **Rate determining step is the dissociative chemisorption of H_2 and D_2**
    (Tafel reaction) (i.e., H_2 activation)

Kinetics of H_2 Exchange and Electro-oxidation*

- Assuming H_2 dissociation step being rate determining in <u>H_2/D_2 exchange</u>:

$$r_{HD} = k_{HD} C_{H_2} (1-\theta)^2 - k_r \theta^2$$

where θ is the coverage of the metal surface by adsorbed H and D at the conditions of exchange (pressure, temperature)

- Assuming the Tafel-Volmer sequence is correct for <u>electrochemical oxidation of H_2</u>:
  - Volmer reaction is the charge transfer step

$$2M + H_2 \rightleftarrows 2HM$$
$$2HM \rightleftarrows 2M + 2H^+ + 2e^-$$

  - Assuming H_2 dissociation being rate limiting, the anodic current density is given by:

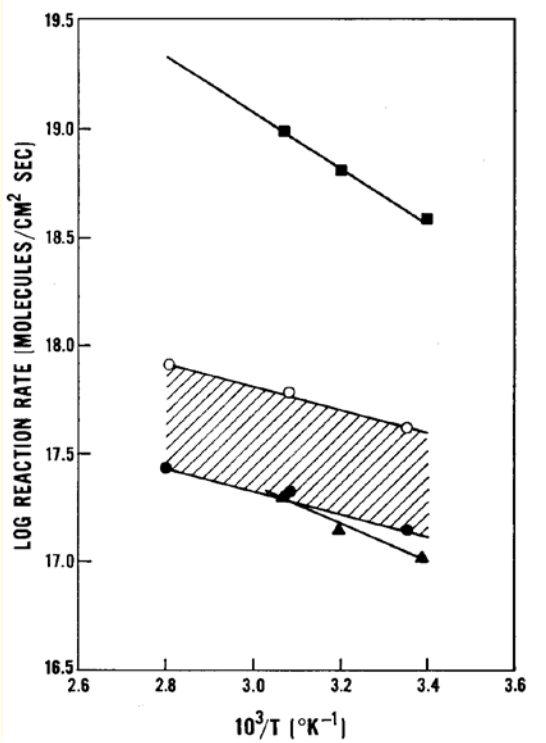
$$i_A = nFk_{at} C_{H_2} (1-\theta)^2 - nFk_{ct}\theta^2$$

where θ is the coverage of the metal surface by adsorbed H, k_{at} and k_{ct} are the anodic and cathodic rate constants

- **<u>Identical kinetic dependence on θ_H</u>**

*Ross, P. N. et al., J. Research Inst. for Catal. 22 (1975) 22-41

H_2/D_2 Exchange vs. Electro-oxidation of H_2



Comparison of rate constants for electrocatalytic oxidation of H_2 molecules on Pt with rate constants for H_2/D_2 Exchange.*

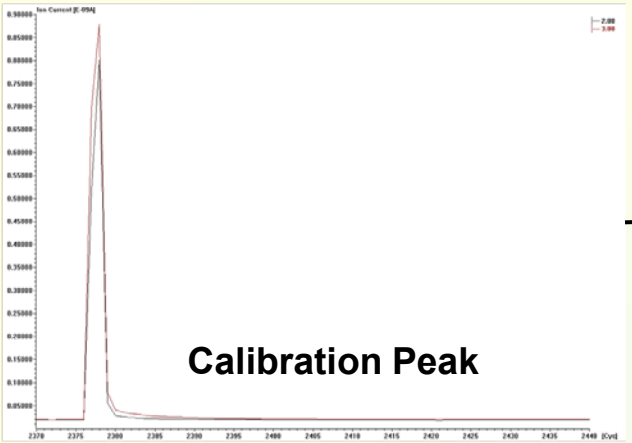
- **Elementary surface reactions on Pt catalysts involving H_2 molecules are the same in both gas-phase and electrochemical catalysis**
- **Rate constants between electrocatalytic oxidation of H_2 on Pt and gas phase H_2/D_2 exchange are almost identical at T = 323 K or 50°C**
- **This suggests a similar rate-determining step between H_2/D_2 exchange and electro-oxidation of H_2 (i.e., H_2 activation) at or close to the temperature indicated.**

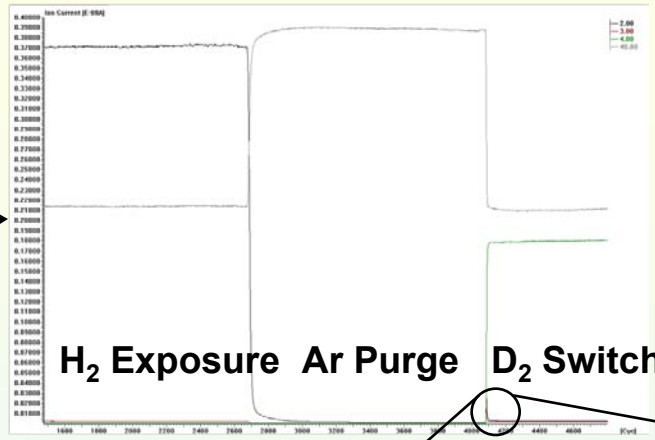
*Ross, P. N. et al., J. Research Inst. for Catal. 22 (1975) 22-41

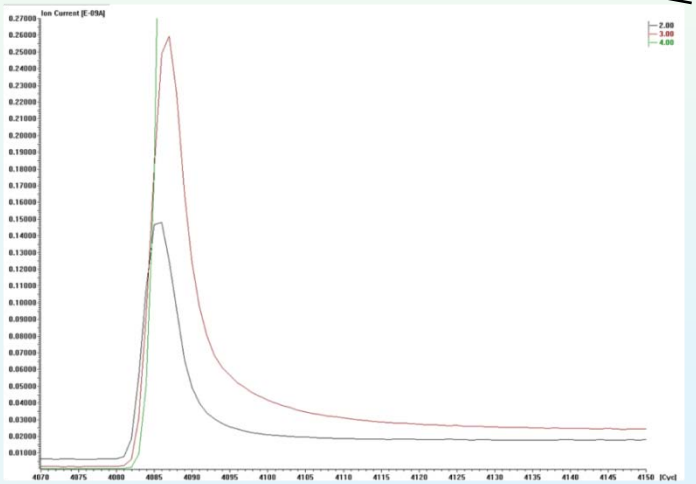
Pros and Cons of H_2/D_2 Exchange versus Cyclic Voltammetry

- **Pros**
  - Direct measurement of H_2 activation on Pt.
  - Can be used in the absence/presence of Nafion®.
  - Poisoning takes place much faster and more uniformly than in a FC.
  - Variation of Pt loading is simple and convenient.
  - Fast experimental time
    - Catalyst powder, once prepared, only needs to be pretreated before reaction.
  - Employment of permeation tubes allow the testing of virtually any impurity.
  - Measure total H surface coverage including H spillover onto the C support.
- **Cons**
  - Poisoning may take place much faster and more uniformly than in a FC.

Hydrogen Surface Concentration Measurements from HDSAP

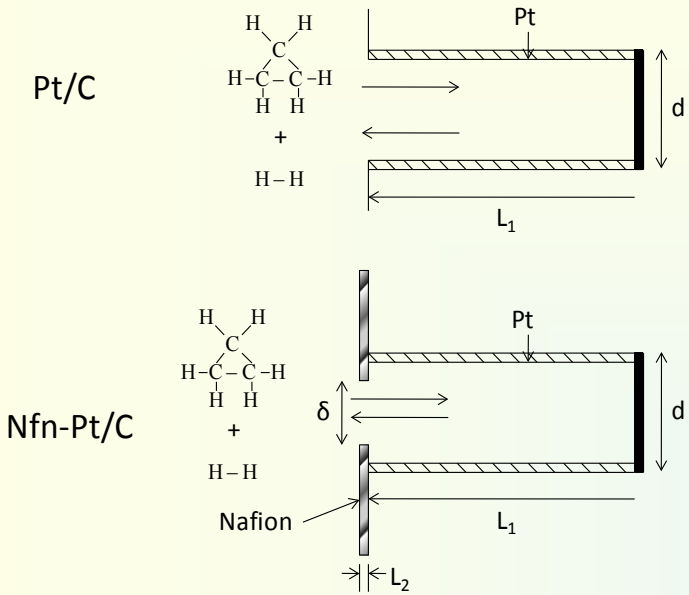


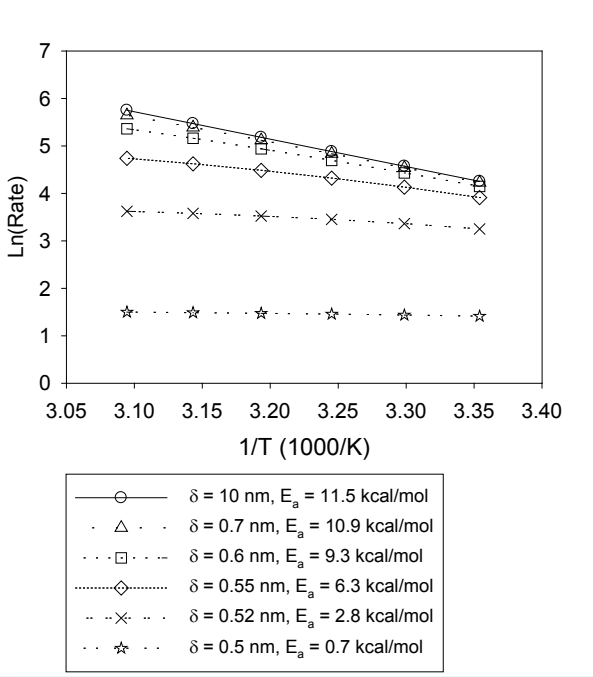




- Calibration Peak – used to calculate, from the HDSAP profile, the concentration of surface hydrogen at TOS.
  - Obtained by flowing known partial pressures of H_2 and D_2 over the catalyst and directing the effluent into a 6-port valve with a 2 mL sample loop. Once the flow is stabilized, the contents within the sample loop is injected into the mass spec.
- After the calibration peak, HDSAP is started by exposing the catalyst to 30 min of H_2 (P_{H2} = 1 atm), purging with Ar for *x* min (*x* = 30 min for Pt/C and 50 min for Nfn-Pt/C), followed by D_2 (P_{D2} = 1 atm) switch via 4-port valve.
- The amount of surface hydrogen is calculated by taking the area under both H2 and HD peaks (with the final leveled off value as background) and comparing them to the area under the calibration peak. The final surface hydrogen concentration is obtained by $(C_{H2} \times 2) + C_{HD}$.

Modeling of impact of effective size of pore opening on E_a of cyclopropane hydrogenolysis on Nafion-Pt/C





- **In the absence of blockage of the pore opening (Pt/C), reaction is rate limited and the E_a is unaffected by diffusion.**
- **Decrease in effective size (δ) of the pore opening (due to Nafion® blockage) does not start to impact the reaction until δ = 0.7 nm.**
- **At δ = 0.5 nm, which is similar to the critical diameter of C_3H_6 (ca. 0.49 nm), the membrane is effectively preventing any C_3H_6 from diffusing into the pore, thus resulting in a E_a close to 0.**
- **Note: the model does not take into account wall effects and electronic interactions.**