

**2010 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, K. Hongirikarn,
and Xunhua Mo
*Clemson University***



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



JOHN DEERE

**Peter Finamoore
*John Deere, Advanced Energy Systems Division***

June 11, 2010

Project ID: FC046

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

- Timeline

- Start: Feb. 15, 2007
- Finish: Feb. 14, 2011
- Completed: 75%

- 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 FY09
 - CU: **\$300,000**
 - SRNL: **\$200,000**
- Funding for FY10
 - CU: **\$314,000**
 - SRNL: **\$175,000**

- 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**

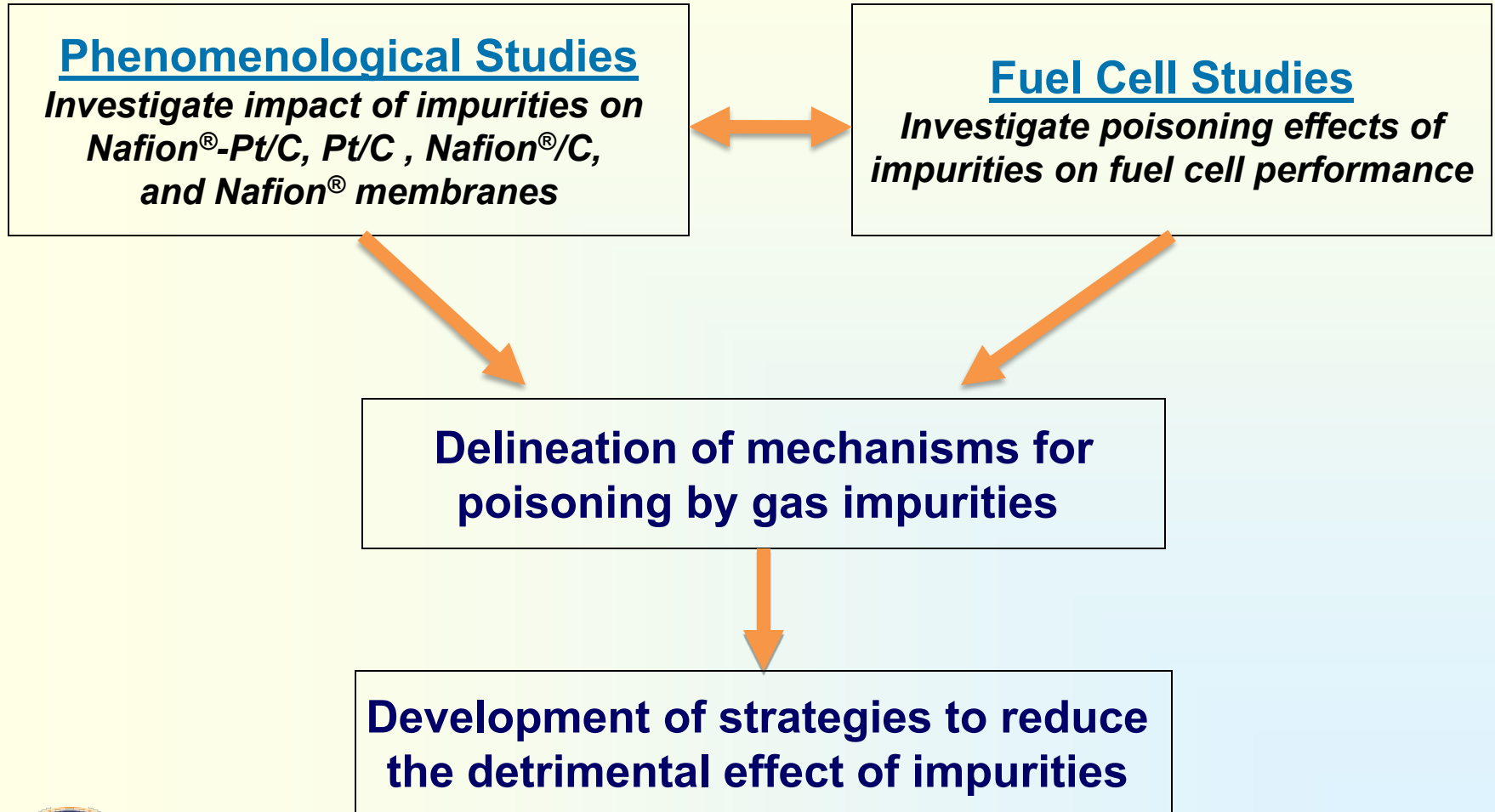
- Investigate in detail the effects of impurities in the hydrogen fuel and oxygen streams on the operation and durability of fuel cells.
 - CO, CO₂, NH₃, H₂O, HCs (incl. C₂H₄, C₂H₆, H₂CO, HCOOH), O₂, inert gases (He, N₂, Ar), Cl₂, and H₂S.
- Determine mechanisms of impurity effects.
- Suggest ways to overcome impurity effects.

- **OBJECTIVES 2009-10**

- 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 and NH₃ poisoning.
 - Complete the study of the prediction of the conductivities of Nafion[®] in the membrane and the catalyst layers based on available proton concentration obtained from esterification.
 - Finalize the study of the effects of different cations (Na⁺, Ca²⁺, and Fe³⁺) and other impurities (CO₂, paraffins, HCOOH, Ar, He and N₂) on Nafion[®] conductivity and H₂ activation on Pt/C and Nafion[®] -Pt/C.
- Fuel Cell Performance Studies
 - Investigate effects of the Cl-containing hydrocarbon (PCE) and THF.
 - Complete long term study of the effect of NH₃ poisoning per DOE request.
 - Complete CO poisoning experiments to correlate and compare results from PEM fuel cell test at SRNL to the results from H₂ activation studies at Clemson.



Technical Approach



Approach

Completed

Milestones

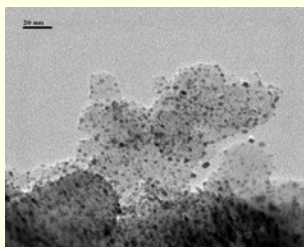
~~AAA~~ Modified

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: <i>ads., TPD, IR</i>	Effect of NH ₃ : <i>pulse ads., IR</i>	Effect of NH ₃ :
3		<i>impact on H₂/D₂ exchange</i>	<i>impact on test reaction (HAc est.)</i>	<i>consideration of protocol modifications</i>
4		<i>impact on H₂-O₂ rxn</i>	<i>conductivity</i>	Effect of CO:
5	Prep. of Nafion® memb.	Effect of NH ₃ :	Effect of CO:	Effect of CO ₂ :
6		Effect of CO ₂ :	Effect of Ethylene:	Effect of Ethylene:
7		Effect of Ethylene:	Effect of CO ₂ :	Effect of Ethane THF:
8		Effect of HCHO:	Effect of Ethane:	Effect of HCHO:
9	Go-No Go Decision	Go-No Go Decision	Go-No Go Decision	Go-No Go Decision
	Prep. of Nafion® membranes for cond. meas.	Effect of Ethane:	Effect of HCHO:	Effect of O₂ Long Term Study of NH ₃ (DOE)
10		Effect of HCOOH:	Effect of O₂ Effect of Na ⁺ , Ca ²⁺ , Fe ³⁺	Effect of HCOOH:
11		Effect of O ₂ :	Effect of HCOOH:	Effect of Cl: TCE
12		Effect of H ₂ O:	Effect of Cl: TCE	Effect of H ₂ O:
13		Effect of Cl ₂ : TCE	Effect of H ₂ O:	Effect of He, Ar, N ₂ :
14		Effect of H ₂ S:	Effect of He, Ar, N ₂ :	Effect of H ₂ S:
15		Effect of He, Ar, N ₂ :	Effect of H ₂ S:	Eff. of Impurity Mixtures
16	FINAL REPORT			

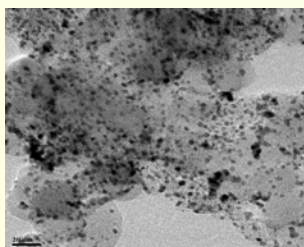


Technical Accomplishments and Progress

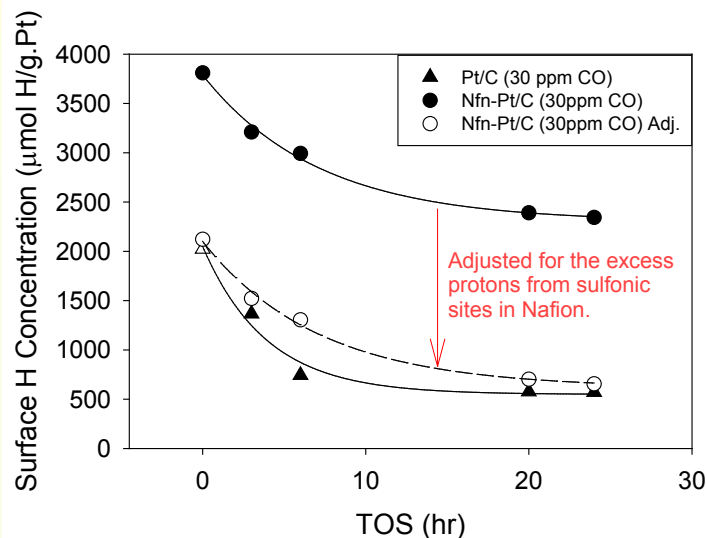
Effect of Nafion[®] on Pt/C



Pt/C



Nfn-Pt/C



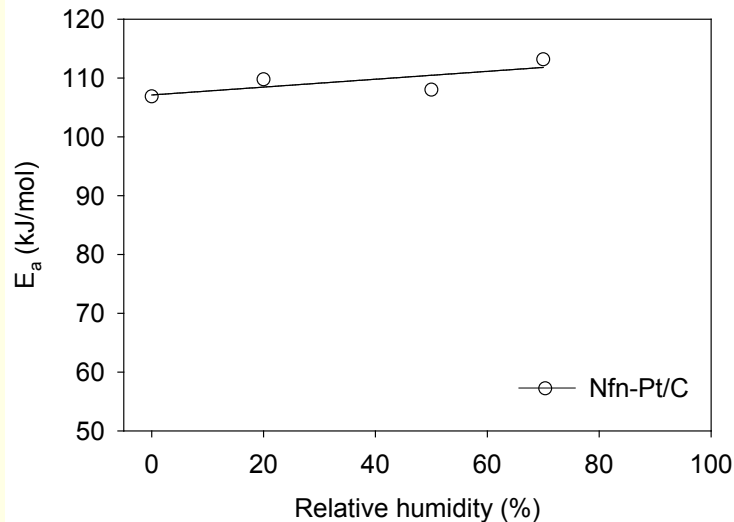
Sample	E_a (kJ/mol)	Rate @ 80°C (μmol HD/g.Pt-sec)
Pt/C (30 ppm CO)	85	1364
Nfn-Pt/C (30 ppm CO)	97	1065

- Addition of Nafion[®] to Pt/C significantly decreases the specific total surface area (BET) of Pt/C but has a negligible impact on the average particle size of Pt.
- No significant difference in amounts of H or CO adsorbed on Pt/C and Nfn-Pt/C, except slight variation in CO (difference in the amounts of bridge-bonded CO?).
- Even though sufficient Nafion[®] is present for a monolayer ca. 0.8 nm in thickness, surface hydrogen measurements, even in the presence of CO, suggest that adsorption of H on Pt is not significantly affected by Nafion[®].
- Nafion[®] appears to have minimal effect on H₂ activation based on apparent E_a and surface hydrogen concentration results.
- There is no effect of Nafion[®] on CO poisoning of Pt/C.

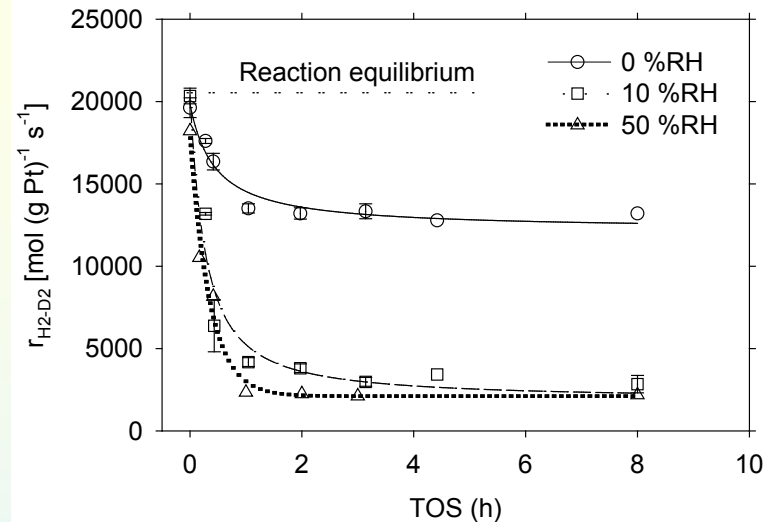


Experimental Conditions: 30 ppm CO in $P_{H_2} = P_{Ar} = 1$ atm, $P_T = 2$ atm, 0 %RH
Apparent E_a : Temperature Range: 50–90°C, Amount of Pt: 0.875 mg Pt
Surface Hydrogen: T = 80°C, Amount of Pt: 17.5 mg Pt

Effect of water vapor on H₂ activation at 80°C



Effect of humidity on E_a for H₂ activation of Nfn-Pt/C in the presence of **10 ppm CO**.

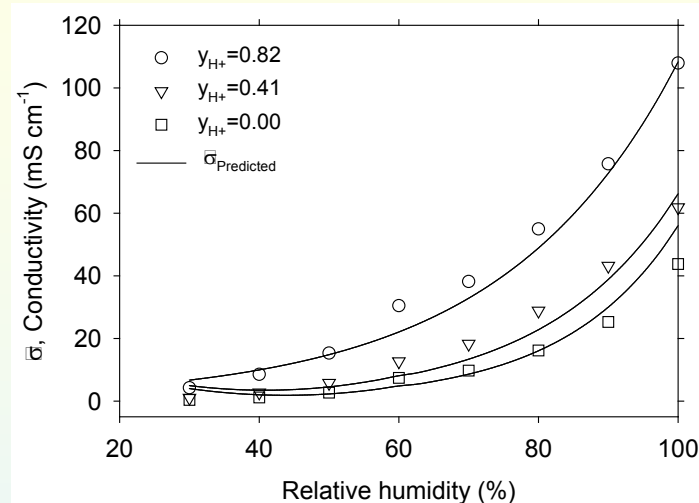
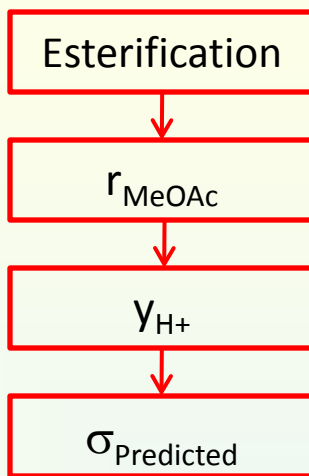
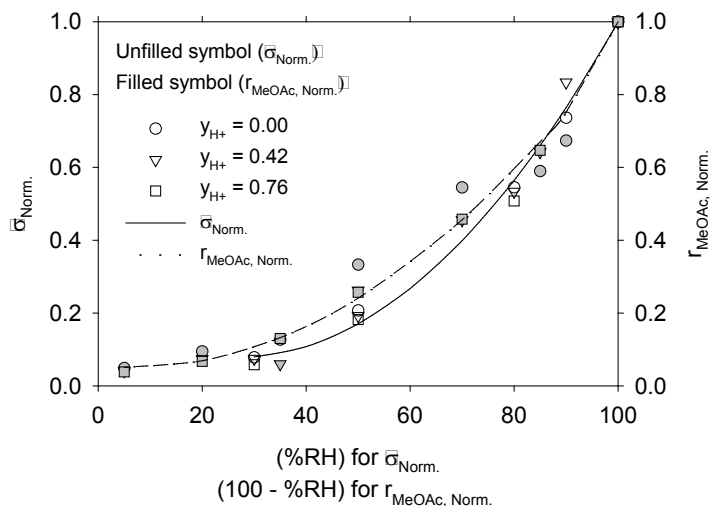


Kinetics of r_{H₂-D₂} of Nfn-Pt/C at 80°C and different humidities in the presence of **10 ppm CO**.

- In absence of a poison like CO, equilibrium still obtained for H₂ activation on Nfn-Pt/C at 80°C in the presence of water vapor.
- Humidity has minimal effect on E_a for H₂ activation on Nfn-Pt/C in 10 ppm of CO at typical FC conditions.
- However, the humidity significantly influences **the degree of poisoning by CO** of Nfn-Pt/C and the final rate of H₂ activation.



Prediction of conductivity of a cationic-contaminated membrane¹



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

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

- Experimental results for NH_3 poisoning (σ and r_{MeOAc}) were used to develop the methodology & correlation.
- $r_{MeOAc, Norm.}$ correlates excellently with $\sigma_{Norm.}$ at fuel cell conditions.

- $\sigma_{Predicted}$ for Na^+ agrees well with experimental results, validating the methodology.

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

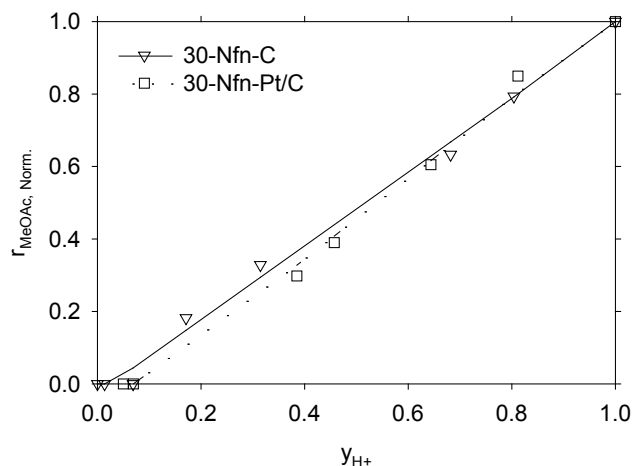
$$\text{Normalized } r_{MeOAc}(r_{MeOAc, Norm.}) = \frac{(r_{MeOAc, y_{H^+}=1} - r_{MeOAc, y_{H^+}})_{RH, 80^\circ C}}{(r_{MeOAc, y_{H^+}=1} - r_{MeOAc, y_{H^+}})_{0\% RH, 80^\circ C}}$$

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

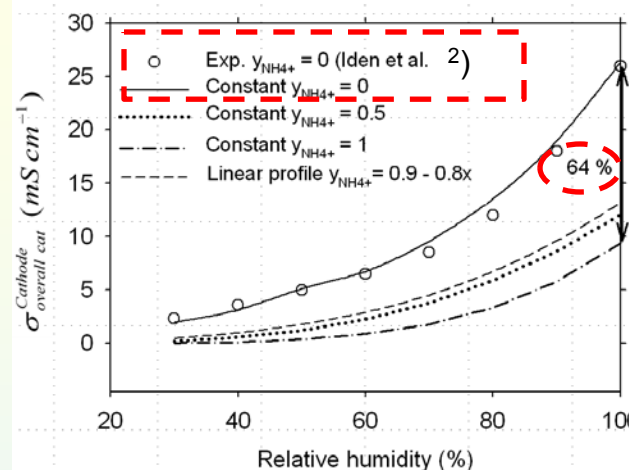


(1) K. Hongsirikarn et al., J. Power sources (195) (2010) 3416.

Prediction of effective conductivity of Nafion® in the catalyst layer¹



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



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

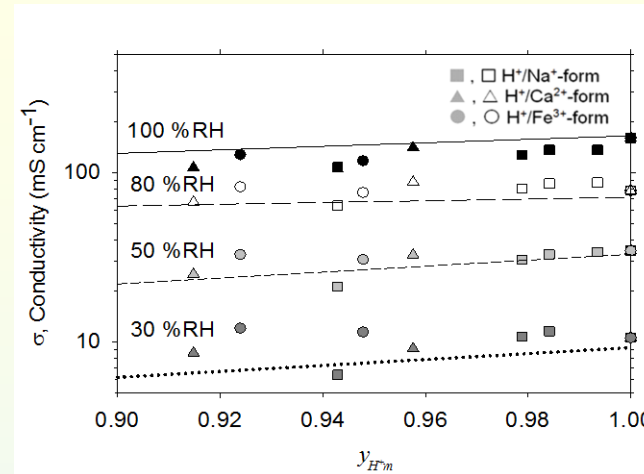
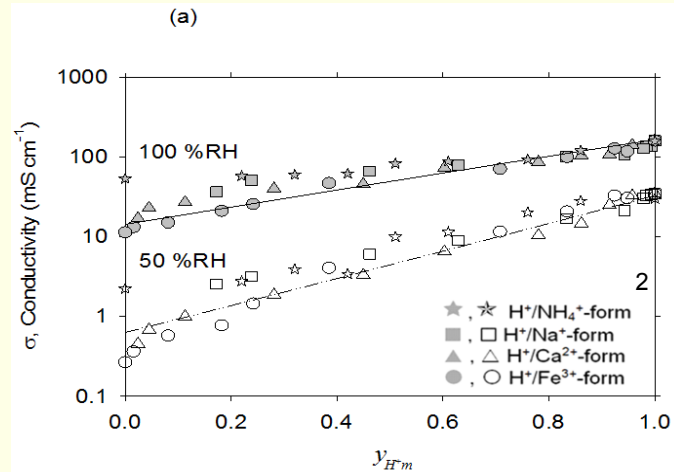
Esterification $\rightarrow y_{H^+} \rightarrow$ an agglomerate model³ $\rightarrow \sigma_{Predicted}$

- $r_{MeOAc, Norm.}$ 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.²
- Predicted $\sigma_{Cathode_{overall\ cat}}$ for the fully NH_4^+ -form was 64% lower than that of the H^+ -form, similar to performance loss in a PEMFC (49-77%)⁴ under equivalent conditions.



(1) K. Hongsirikarn et al., J. Power Sources, In press 2010
 (2) H. Iden et al., J. Electrochem. Soc. 156 (9) (2009) B1078
 (3) F. Jaouen et al., J. Electrochem. Soc. 149 (4) (2002) A437
 (4) Uribe et al., J. Electrochem. Soc. 149 (3) (2002) A293

Effect of cations (Na^+ , NH_4^+ , Ca^{2+} , Fe^{3+}) on Nafion[®] membrane conductivity¹



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

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

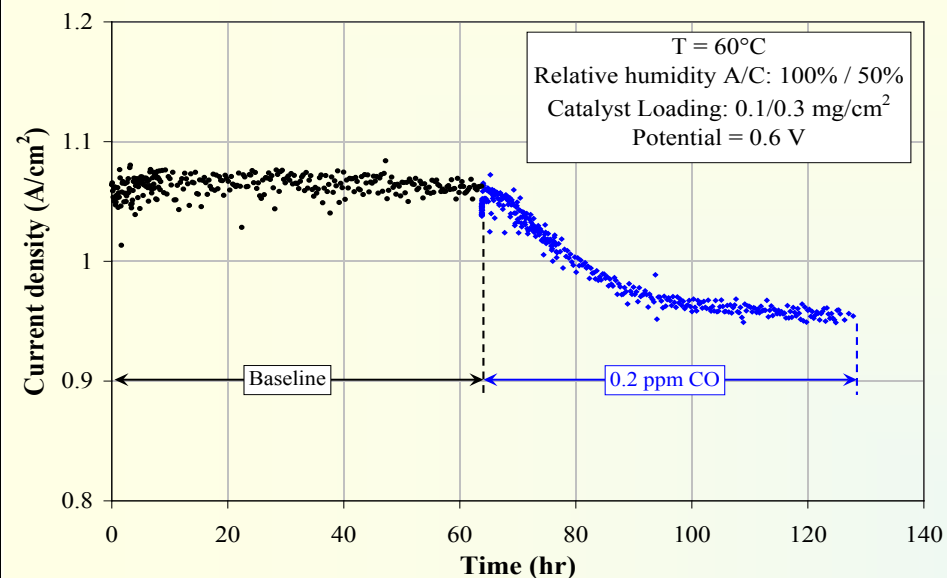
- At the same y_{H^+} , the conductivities of membranes poisoned with monovalent cations (i.e., Na^+ , NH_4^+) were similar, but slightly higher than those with higher valent cations (Ca^{2+} , Fe^{3+}).
- The effect of cations on the conductivity of a membrane having trace amounts of cations was minimal and was proportional to y_{H^+} .
- 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.



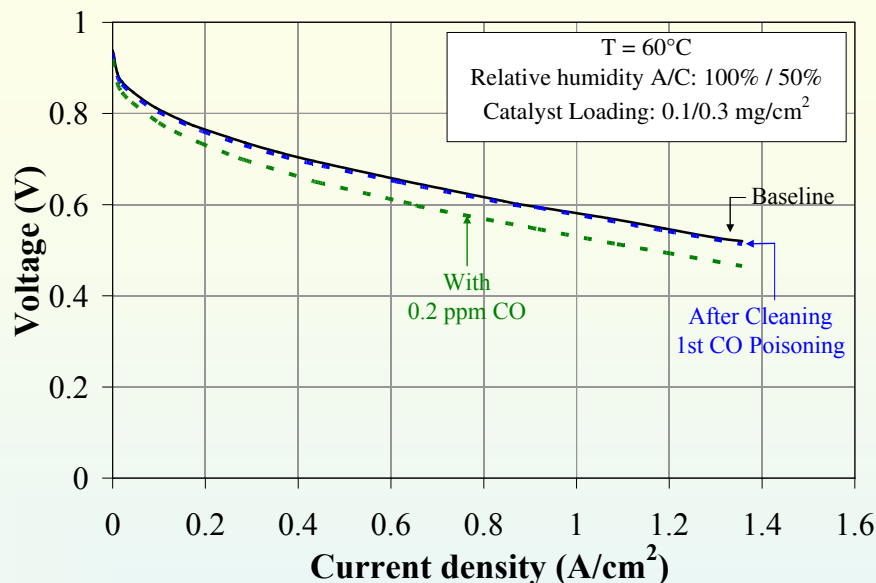
(1) K. Hongsirikarn et al., J. Power Sources, under review (2010)
 (2) K. Hongsirikarn et al., J. Power sources (1) (2010) 30

Technical Accomplishments and Progress

Effects of 0.2 ppm CO on FC Performance



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

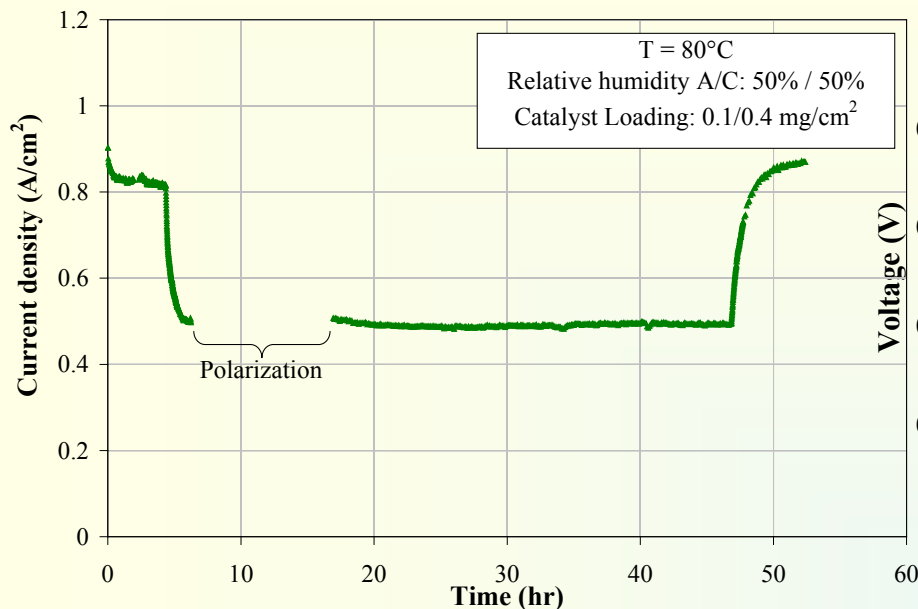


Cell Performance

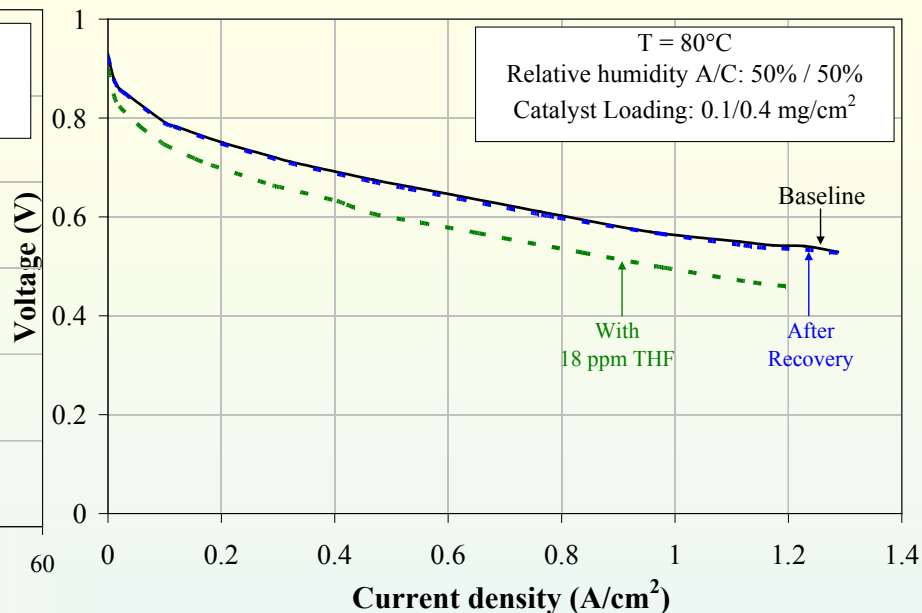
- ~8% of performance is lost in 30 hours after cell is exposed to 0.2 ppm of CO.
- Complete recovery is observed after CV.



Effects of 18 ppm THF on FC Performance



Poisoning with 18 ppm THF and Recovery

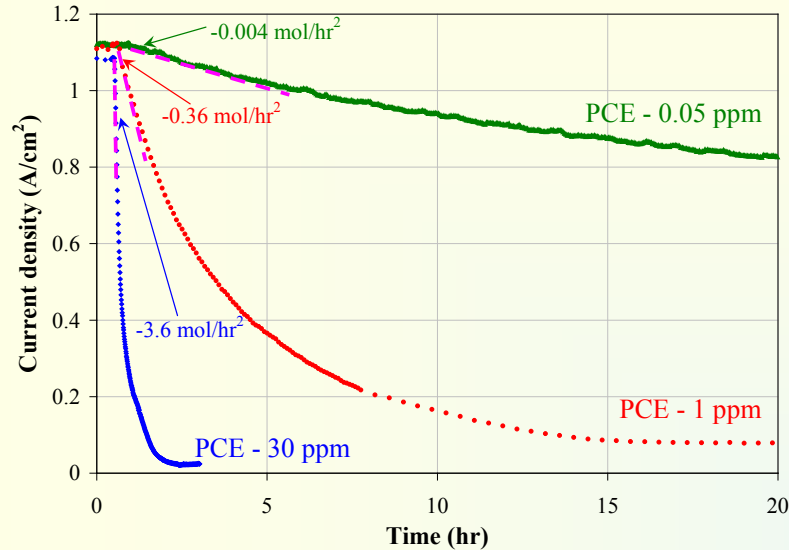


Cell Performance

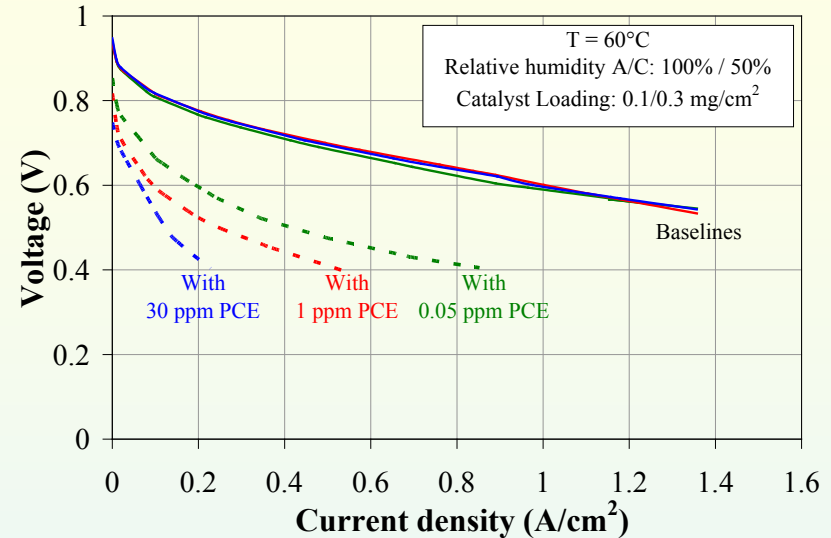
- Tetrahydrofuran (C₄H₈O, THF) has been used to characterize the performance effects that hydrocarbons can have on fuel cell performance.
 - THF is a popular solvent used in many chemical synthesis which include hydrogen storage materials.
- Approximately 40% loss in performance is observed.
- Full recovery is observed as soon as THF is removed from the fuel stream.



PCE cell poisoning at 0.6 V



Poisoning with PCE at 0.6 V



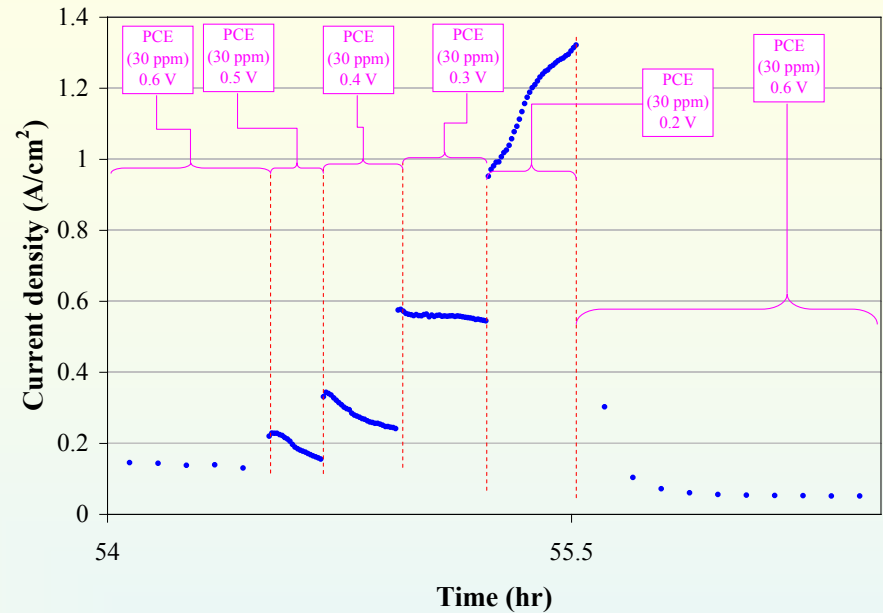
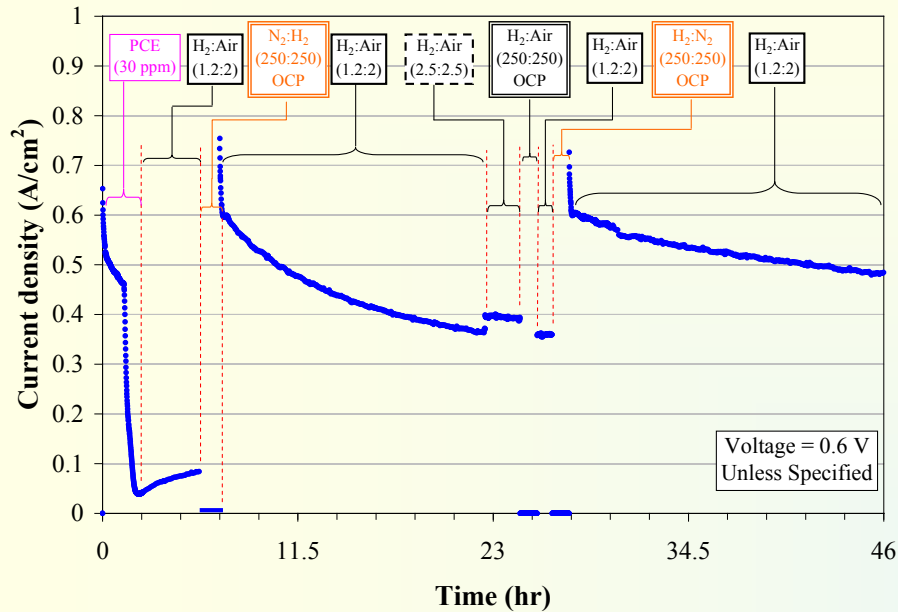
Cell Performance after steady state poisoning

- 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.



Technical Accomplishments and Progress

PCE performance recovery studies



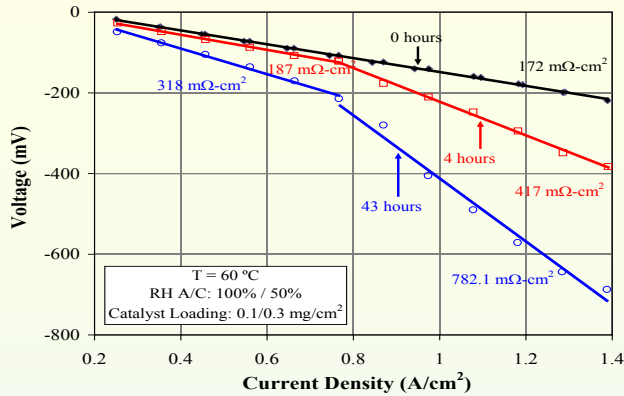
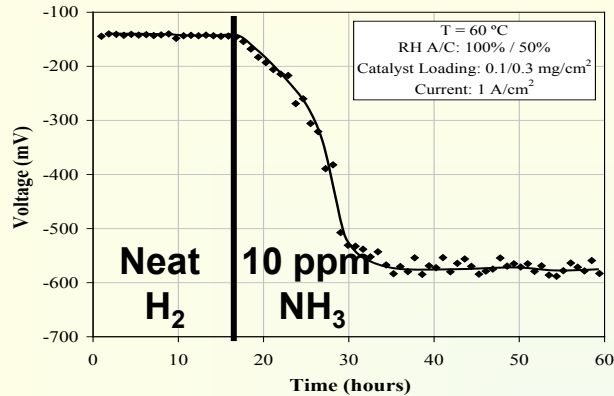
Recovery under different operating conditions

Cell Performance under different operating voltages

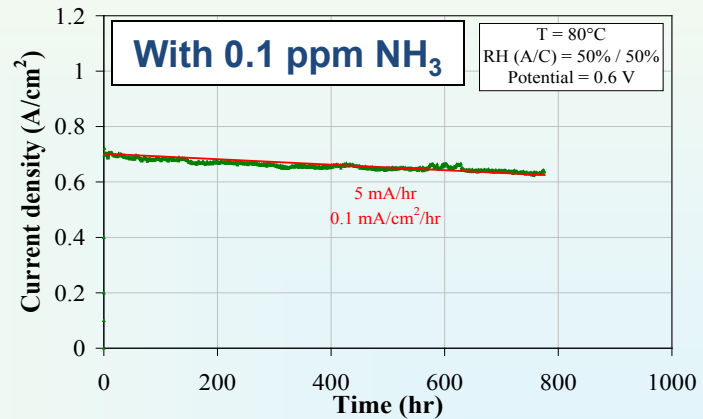
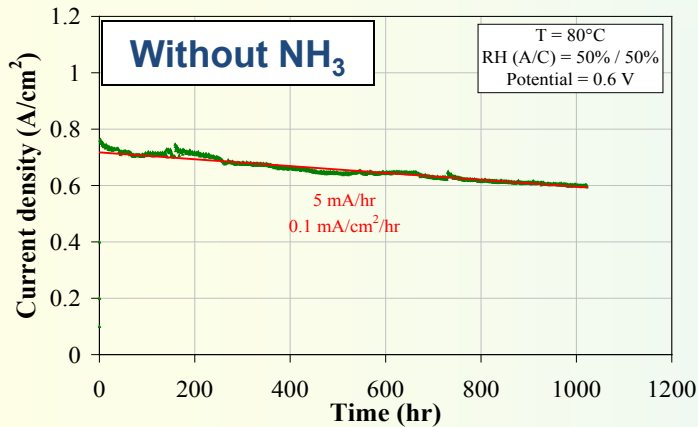
- Best recovery was when N₂:H₂ was used for Anode:Cathode during OCP.
- No effect was observed with increasing of gas flow during normal operation.
- PCE shows no effect on performance when cell uses H₂:Air at low voltages.
- Complete recovery is observed after extended shutdown with N₂ purge.



Effects of NH₃ at the maximum ISO specified level



Effect of 10 ppm NH₃ on Membrane & Ionomer @ 60 °C



Effect of 0.1 ppm NH₃ on Gore MEA @ 80 °C

- At 0.1 ppm, NH₃ does not affect baselines of Gore and Ion Power MEAs.



Technical Accomplishments and Progress

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	TBD	No
Acetaldehyde	TBD	250 ppm	0.00025	TBD	No
Perchloroethylene	Major	400 ppm	0.0004	TBD	No
Tetrahydrofuran (THF)	Yes	400 ppm	0.0004	TBD	No
Propane (C ₃ H ₈)	No	100 ppm	0.0001	Minimal	No
Butane (C ₄ H ₁₀)	No	100 ppm	0.0001	Minimal	No
Pentane (C ₅ H ₁₂)	No	100 ppm	0.0001	Minimal	No
Hexane (C ₆ H ₁₄)	No	100 ppm	0.0001	Minimal	No
Heptane (C ₇ H 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)



Technical Accomplishments and Progress
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.
- Since during CO poisoning, CO does not fully cover all the Pt sites regardless of CO concentration, in order to maintain better fuel cell performance, the use of higher loadings of Pt is recommended if better CO-resistant catalysts are not available.
- Preliminary data suggest that in the presence of CO, lower humidity appears to decrease the effect of CO poisoning on Pt. Thus, lower humidity is recommended in order to minimize CO poisoning on Pt.

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 H₂ Prog.

- *Ex-situ* characterization of Pt/C, Nafion®-Pt/C, and Nafion® membrane.
- Investigation of effect of poisoning of the Pt catalyst on H₂ activation using H₂-D₂ 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 H₂ 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 (2010-2011)

- **Activities**

- Complete the studies of the effect of CO and NH₃ in the presence of water vapor on H₂ activation on Pt/C and Nafion[®]-Pt/C.
- Complete the studies of the effects of PCE, CO₂, ethane, and ethylene on fundamental processes (on Nafion[®]-Pt/C) and fuel cell performance to understand poisoning mechanisms and rates.
- Complete CO poisoning studies at SRNL to correlate and compare results from PEM fuel cell test at SRNL to mass spectrometer results from H₂/D₂ exchange experiments at Clemson.
- Work with DOE H₂ Fuel Quality Working Group to Support ISO Standard Process.
- Provide Argonne Nat. Lab Modeling Group with phenomenological data on NH₃ poisoning of Nafion[®] and CO and PCE poisoning of Pt.
- Develop strategies for mitigating the effects of FC poisons.

- **Upcoming Milestones**

- Complete phenomenological studies of effects of CO, NH₃, and PCE on Nafion[®]-Pt/C and in the presence of water vapor.
- Complete phenomenological studies of effects of CO₂, acetaldehyde, and ethylene on Pt/C and Nafion[®]-Pt/C.
- Complete FC runs of effects of CO, NH₃, CO₂, PCE and acetaldehyde on FC performance.
- Correlate phenomenological results with actual FC runs.

- **Decision Points** None



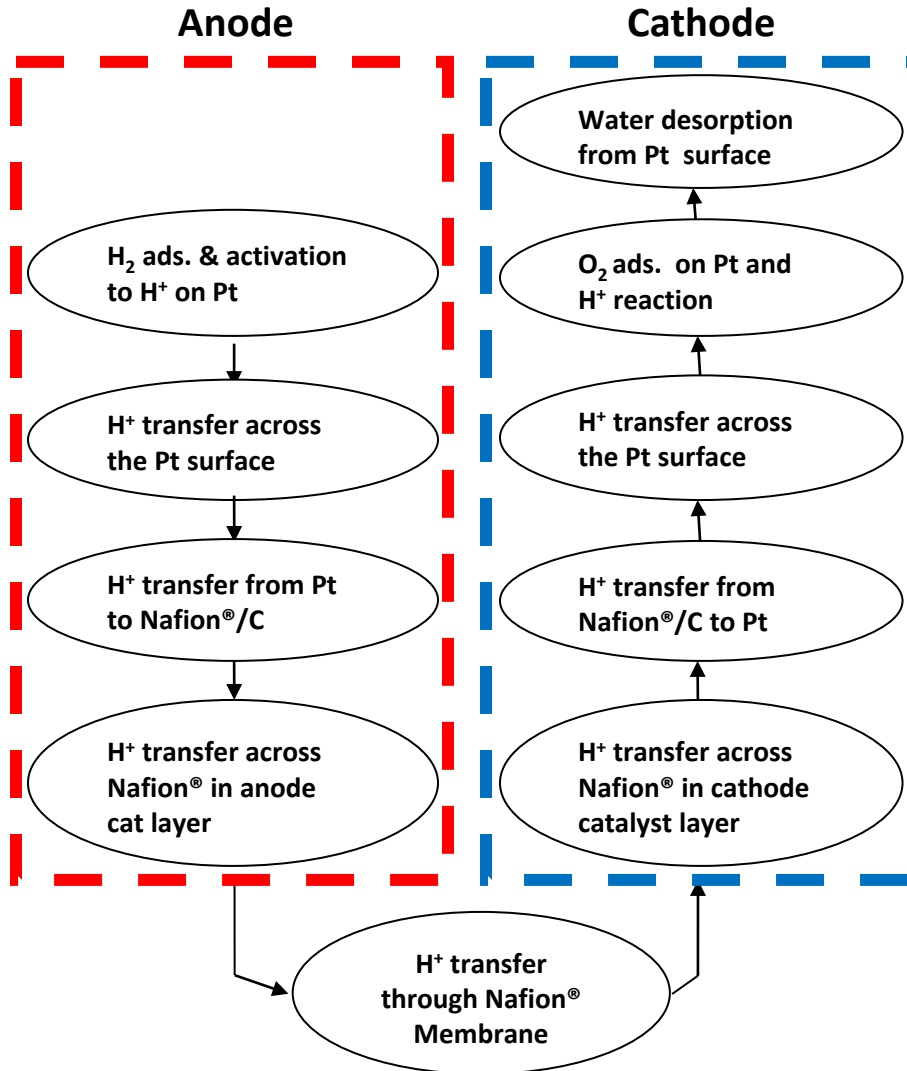
Summary

- The effects of CO₂, C₂-C₇ paraffins, HCOOH and N₂ on Nafion[®] conductivity or Pt for H₂ activation were insignificant.
- A simple acid catalyzed reaction (esterification) can be used to quantitatively predict conductivity of a contaminated membrane and/or catalyst layer under typical fuel cell conditions.
- The surface concentration of hydrogen on Nfn-Pt/C under fuel cell operation conditions was obtained using H₂/D₂ switching and it was found that
 - hydrogen activation occurred only on Pt.
 - transport of protons from the sulfonic sites of Nafion[®] to the Pt particles was extremely fast.
- Humidity has a minimal effect on E_a of H₂ activation for Pt/C under typical FC conditions. However, the humidity significantly influences the degree of poisoning on Nfn-Pt/C and the final rate of H₂ activation.
- 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.
- Preliminary studies on the impact of perchloroethylene (PCE) indicate that PCE affects the cell mostly at high potentials.
- Investigation of the long-term NH₃ poisoning with NH₃ at 0.1 ppm found no appreciable degradation at 60°C and 80°C with the introduction of NH₃ at the maximum ISO specified level.
- CO poisoning experiments were performed to correlate and compare results from PEM fuel cell tests at SRNL to the results from H₂ activation on Nfn-Pt/C experiments at Clemson.



Supplemental Slides

Rate Steps during FC Operation



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

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)
- ❑ H₂ Chemisorption (Pt/C, Naf-Pt/C)
- ❑ Acid site titration (Nafion[®], Naf-Pt/C)
- ❑ NH₃ ads. to meas. BA sites (Nafion[®], Naf-Pt/C)
- ❑ TPD (Pt/C, C)

❑ Reaction Characterization

- ❑ H₂-D₂ (Pt/C, Naf-Pt/C)
- ❑ H₂-O₂ (Pt/C, Naf-Pt/C)
- ❑ Model BA-catalyzed reaction (Nafion[®], Naf-Pt/C)

❑ Conductivity Measurement

- ❑ Impedance analysis (Nafion[®], Naf-Pt/C)

SRNL



Impurity Mixture Generator
(Up to 48 impurities at the time)

❑ 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



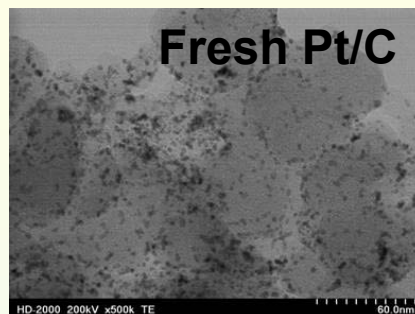
Temperatures	80° C
Pressure	1 bara (P _a =P _c)
Humidity	100 % RH anode, 50 % RH cathode
Stoichiometry (A/C)	H ₂ /Air = 1.2/2.0 @ 0.6 V
Pt Loading	Anode 0.1 mg Pt/cm ² (20 wt% Pt-C)
	Cathode 0.3 mg Pt/cm ² (40 wt% Pt-C)
Electrolyte	Nafion [®] 212
Cell Area	50 cm ²



Technical Accomplishments and Progress

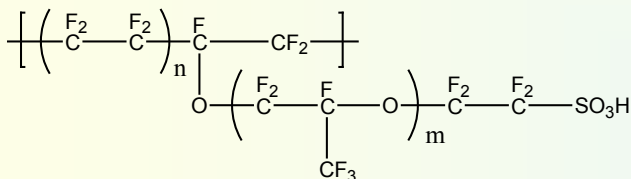
Experimental: Materials

- **Anode: 20 wt% Pt/C (E-TEK)**
 - Pt Particle Size: 22 Å (E-TEK)
 - BET Surface Area: 128 m²/g (E-TEK)
- **Cathode: 40 wt% Pt/C (E-TEK)**
 - Pt Particle Size: 29 Å (E-TEK)
 - BET Surface Area: 100 m²/g (E-TEK)
- **5 wt% Nafion® EW 1100 Solution (Ion Power)**



Surface concentration (EDX)

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



- **Carbon Black Powder (XC-72R, Cabot)**
 - BET Surface Area: 250 m²/g (Cabot)
- **30 wt% Naf / 20 wt% Pt/C (prepared)**
 - Nafion® supported on Pt/C is prepared via incipient wetness impregnation of the commercial 20 wt% Pt/C (E-TEK) with Nafion® ionomer solution (LQ-1105, DuPont, 5 wt.% Nafion®) with an optimum Nafion® content of ca. 30 wt%.
- **MEAs (Ion Power)**
- **Nafion® 212 Membrane EW 1100 (DuPont)**

Measured Values

BET Surface Area:

- C Support: 226 m²/g
- 20 wt% Pt/C: 182 m²/g
- 30 wt% Nafion®/C: 59 m²/g
- 30 wt% Nfn-Pt/C: 62 m²/g

Acid Site Density:

- 30 wt% Nafion®/C: 267 μmol/g
- 30% Nfn-Pt/C: 255 μmol/g



Technical Accomplishments and Progress

H₂/CO Chemisorption Results for Pt/C and Nfn-Pt/C

Sample	Absorbate	Analysis Condition	Amount of H or CO adsorbed		Metal Dispersion (%)
			($\mu\text{mol/g.cat}$)	($\mu\text{mol/g.Pt}$)	
Pt/C	H ₂	35°C	316	1806	35
	H ₂	80°C	361	2063	40
	CO	35°C	292	1669	33
	CO	80°C	297	1697	33
Nfn-Pt/C	H ₂	35°C	255	1861	36
	H ₂	80°C	296	2160	42
	CO	35°C	199	1452	28
	CO	80°C	199	1452	28

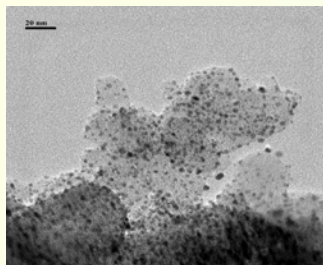
- When the uptake results are scaled from per gram of catalyst to per gram of Pt, the amounts of hydrogen uptake and the metal dispersions for Pt/C and Nfn-Pt/C are comparable, within experimental error.
- The slight variation in CO uptake between the two catalysts may be due to a difference in the amount of bridge-bonded CO.



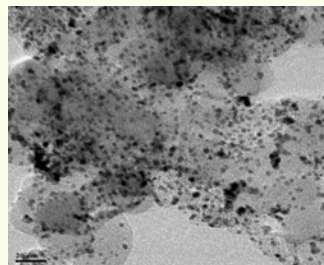
Technical Accomplishments and Progress

Effect of Nafion[®] on the Characteristics of Pt/C

BET surface area, pore volume, and pore size of carbon support, Pt/C, and Nafion[®]-Pt/C



Pt/C



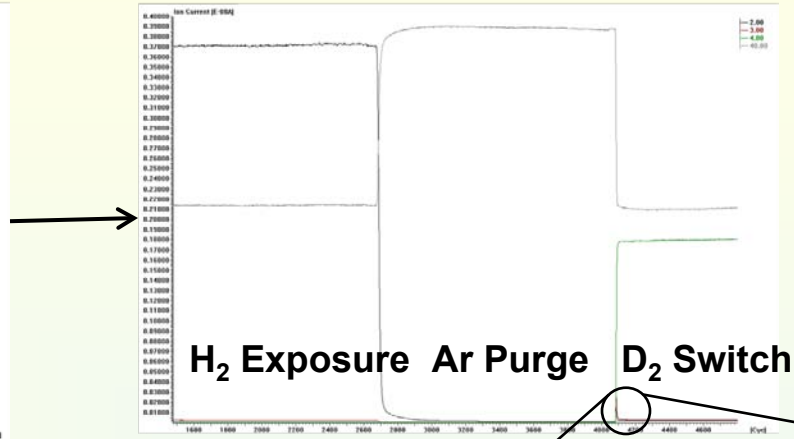
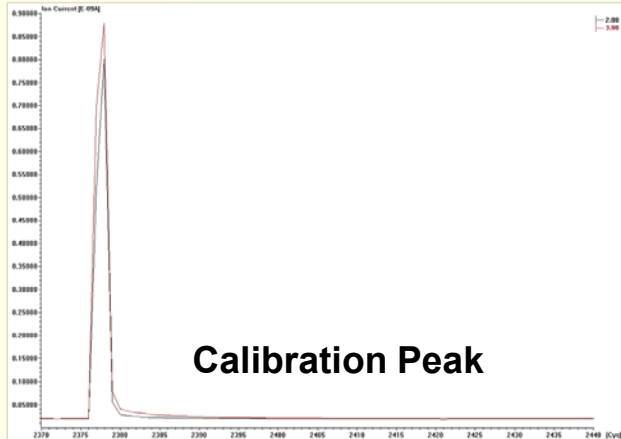
Nfn-Pt/C

Sample	Surface Area (m ² /g.cat)	Pore Volume (cm ³ /g.cat)	Pore Size (Å)
XC-72	225	0.63	164
Pt/C	170	0.44	159
Nfn-Pt/C	37.4	0.28	327

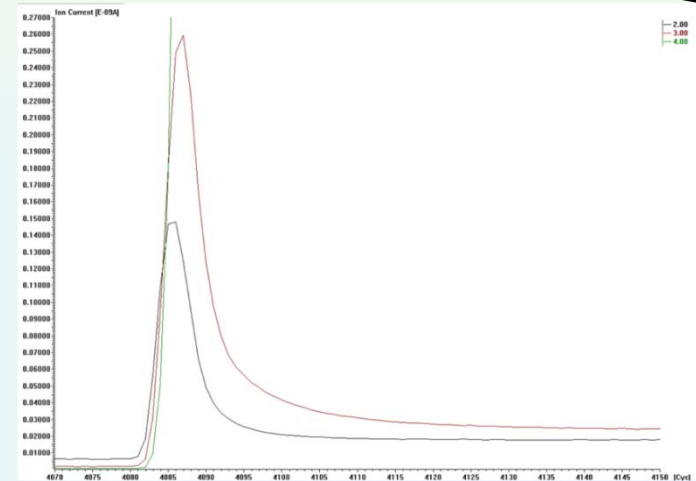
TEM images of Pt (20 wt%)/C and Nfn(30 wt%)-Pt/C

- The BET and TEM results of Nfn-Pt/C indicated that the addition of Nafion[®] to Pt/C severely decreases the specific total surface area of Pt/C but has a negligible impact on the average particle size of Pt.
- The static H₂/CO chemisorption analysis found no significant difference in amounts of H or CO adsorbed on Pt/C and Nfn-Pt/C, except a slight variation in CO uptake, which may be due to a difference in the amounts of bridge-bonded CO.

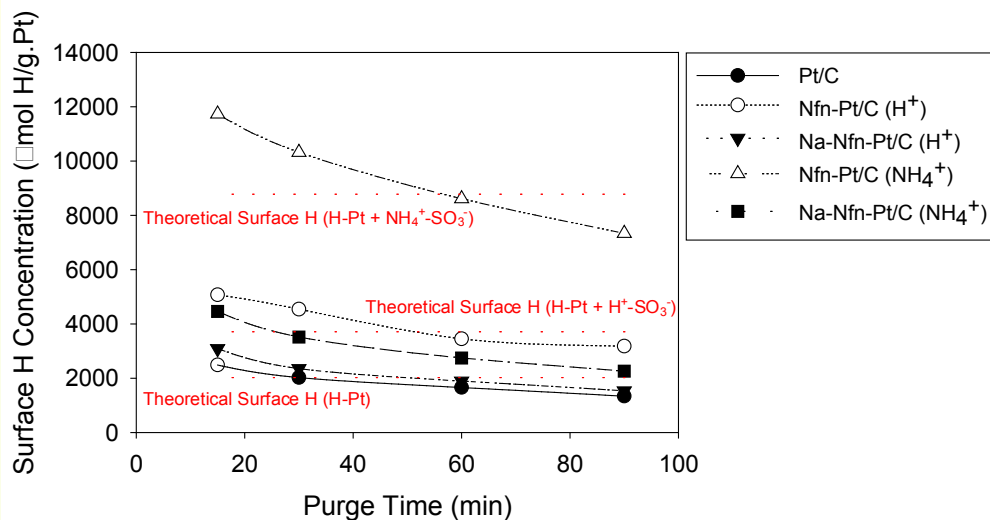
Hydrogen Surface Concentration Measurements from HDSAP



- Calibration Peak – used to calculate, from the HDSAP profile, the concentration of surface hydrogen at TOS.
 - Obtained by flowing known partial pressures of H₂ and D₂ 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 H₂ ($P_{H_2} = 1$ atm), purging with Ar for x min ($x = 30$ min for Pt/C and 50 min for Nfn-Pt/C), followed by D₂ ($P_{D_2} = 1$ 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 $(C_{H_2} \times 2) + C_{HD}$.



Effect of Purge Time on Hydrogen Surface Concentration

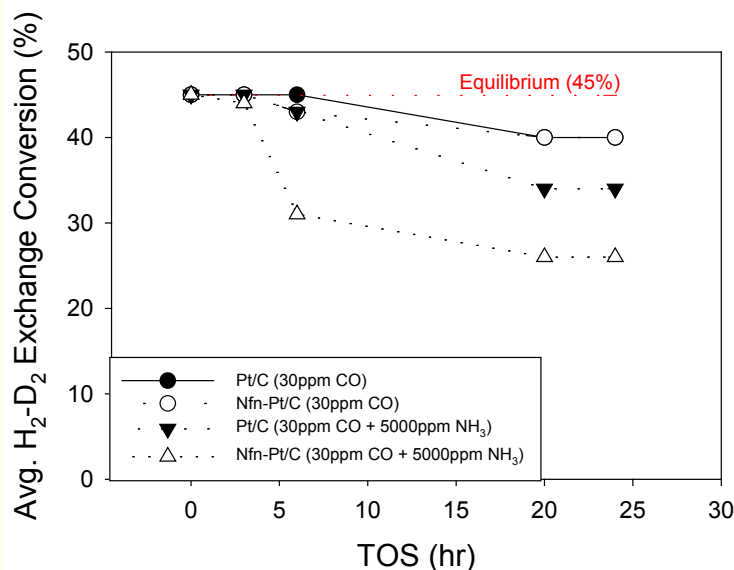


- Results from H₂/CO chemisorption suggest a surface Pt-H concentration of ca. 2023 μmol H/g.Pt for Pt/C at 80°C.
- Due to the exchange between hydrogen and deuterium during HDSAP, hydrogen associated with the sulfonic sites present in Nafion[®] increases the hydrogen surface concentration measured by a theoretical amount of 1688 μmol H/g.Pt. (Pt_H + H-SO₃ = 3711 μmol H/g.Pt).
- Poisoning of the sulfonic sites in Nafion[®] with Na⁺ cation (Na-Nfn-Pt/C) significantly decreased hydrogen surface concentration compared to Nfn-Pt/C (H⁺) and closer to that of Pt/C. Results suggest 4.5 out of 5.5 sulfonic sites have been poisoned with Na⁺.
- Exposure of Nfn-Pt/C to NH₃ increased the amount of exchangeable hydrogen from Nafion[®] from 1 hydrogen per sulfonic site to 4 hydrogen atoms per sulfonic site due to the formation of NH₄⁺-SO₃⁻. (Pt_H + NH₄⁺-SO₃⁻ = 8775 μmol H/g.Pt). Exposure of Pt/C to NH₃ showed little effect on surface hydrogen concentration.



Technical Accomplishments and Progress

Effect of NH₃ on CO poisoning on Pt/C and Nfn-Pt/C*



Hydrogen Activation at 80°C

Sample	App. E _a (kJ/mol)	Rate @ 80°C (μmol HD/g.Pt-sec)
Pt/C (30 ppm CO)	85	1364
Nfn-Pt/C (30 ppm CO)	97	1065
Pt/C (30 ppm CO + 5000 ppm NH ₃)	85	896
Nfn-Pt/C (30 ppm CO + 5000 ppm NH ₃)	83	459

- Nafion[®] did not appear to impact H₂ activation in the presence of CO only.
- Exposure to CO + NH₃ not only decreased H₂ activation on Pt/C, but had an even more detrimental effect on Nfn-Pt/C.
- While the exposure of Pt/C and Nfn-Pt/C to CO + NH₃ results in a 1.5X and 2.3X lower rate of H₂ activation than with just CO, respectively, the synergistic poisoning effect between CO + NH₃ and their interactions with Pt appears to have a negligible effect on the apparent E_a.



*Experimental Conditions

Flows: 30 ppm CO + (30 or 5000) ppm NH₃ in P_{H₂} = P_{Ar} = 1 atm; Total Pressure: 2 atm; 0 %RH

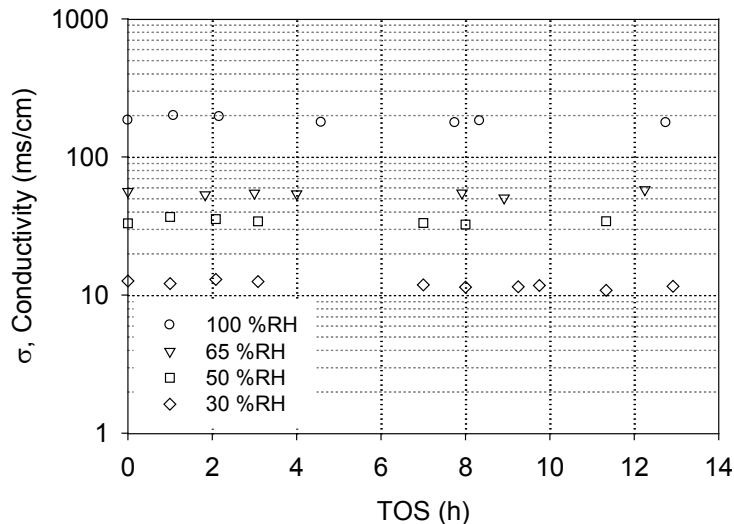
Apparent E_a: Temperature Range: 50 – 90°C, Amount of Pt: 0.875 mg Pt

Avg. H₂-D₂ Conversion vs TOS: Temperature: 80°C, Amount of Pt: 17.5 mg Pt

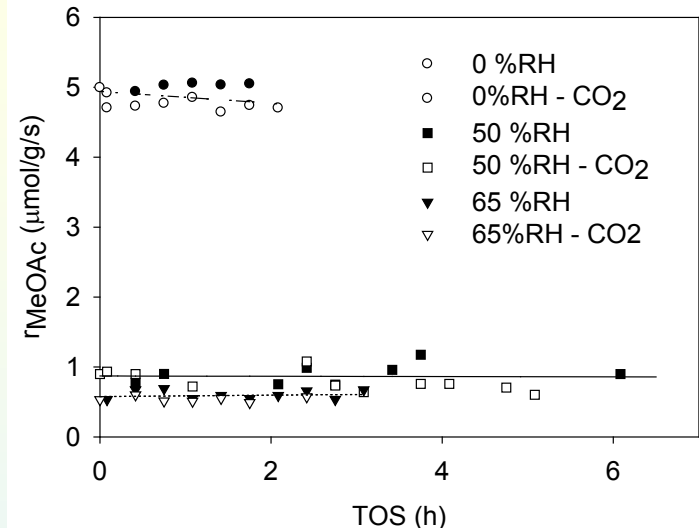


Technical Accomplishments and Progress

Effect of Other Impurities on Nafion[®] Conductivity and Esterification Activity at 80°C



Conductivity of a Nafion[®] membrane in the presence of 500 ppm CO₂ at 80°C.

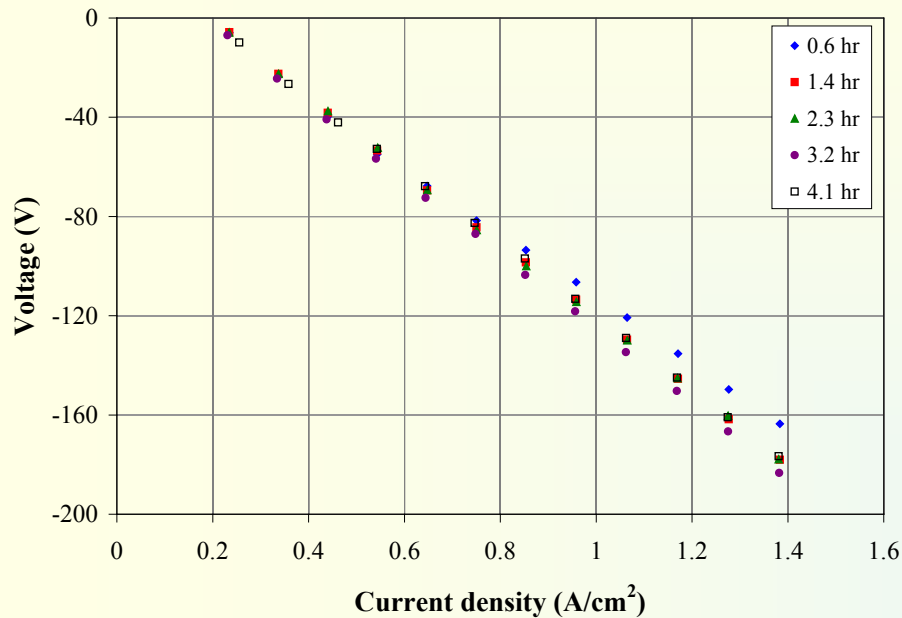


Esterification activity of a Nafion[®] membrane in the presence of 500 ppm CO₂ at 80°C.

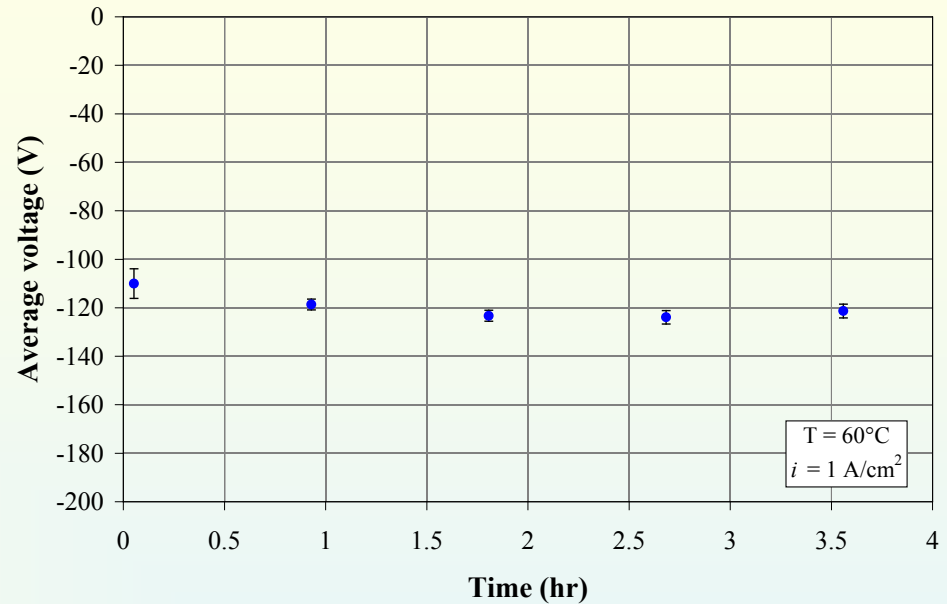
- It was found that CO₂ has no effect on the Nafion[®] conductivity or on the esterification activity under these conditions.
- In addition, exposure of the Nafion[®] membrane to either 50 ppm CO or 500 ppm perchloroethylene at 80°C for 12 h doesn't influence either Nafion[®] conductivity or r_{MeOAc} (data not shown here).
- These observations provide further evidence to justify the use of esterification to quantitatively investigate proton availability and to predict the conductivity of Nafion[®] polymer or other proton conductive materials.



H₂ Pump Experiment with 30 ppm PCE Poisoning



Polarization H₂ pump section



Overpotential at 50 A (1 A/cm²) H₂ pump

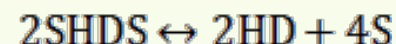
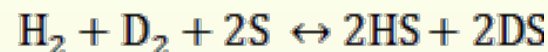
- No effects on the overpotential are observed in the hydrogen redox reaction or membrane resistance even with 30 ppm PCE exposure.



H₂/D₂ Exchange Mechanism

- H₂/D₂ 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

- In the temperature region indicated

- Rate of surface diffusion is very rapid
- Rate determining step is the dissociative chemisorption of H₂ and D₂
(Tafel reaction) (i.e., H₂ activation)



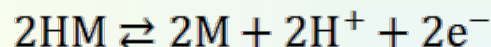
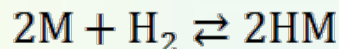
Kinetics of H₂ Exchange and Electro-oxidation*

- Assuming H₂ dissociation step being rate determining in H₂/D₂ exchange:

$$r_{\text{HD}} = k_{\text{HD}} C_{\text{H}_2} (1 - \theta)^2 - k_r \theta^2$$

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 electrochemical oxidation of H₂:
 - Volmer reaction is the charge transfer step



- Assuming H₂ dissociation being rate limiting, the anodic current density is given by:

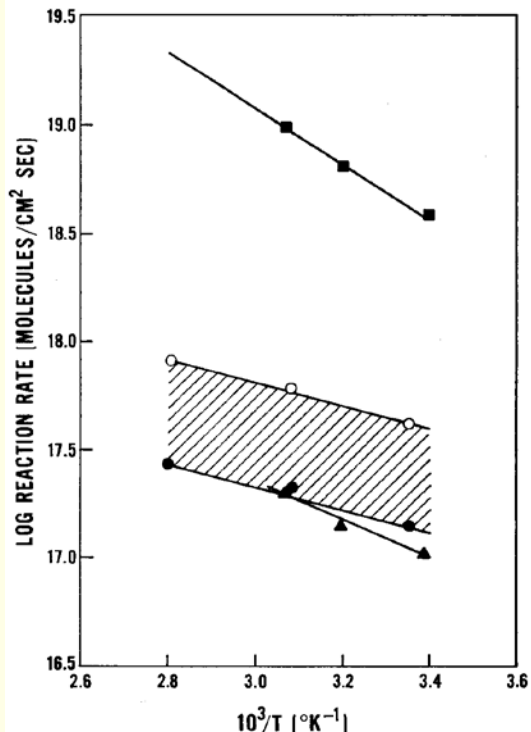
$$i_{\text{A}} = nFk_{\text{at}} C_{\text{H}_2} (1 - \theta)^2 - nFk_{\text{ct}} \theta^2$$

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

- Identical kinetic dependence on θ_{H}



H₂/D₂ Exchange vs. Electro-oxidation of H₂



- , Electrocatalytic adsorbed hydrogen atom oxidation (VOLMER reaction, real surface area)
- ▲, Electrocatalytic hydrogen molecule oxidation (real surface area)
- , H₂-D₂ exchange (geometric area)
- , H₂-D₂ exchange ("real" surface area from electrochemical determination of Pt site density).

Comparison of rate constants for electrocatalytic oxidation of H₂ molecules on Pt with rate constants for H₂/D₂ Exchange.*

- Elementary surface reactions on Pt catalysts involving H₂ molecules are the same in both gas-phase and electrochemical catalysis
- Rate constants between electrocatalytic oxidation of H₂ on Pt and gas phase H₂/D₂ exchange are almost identical at T = 323 K or 50°C
- This suggests a similar rate-determining step between H₂/D₂ exchange and electro-oxidation of H₂ (i.e., H₂ 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 H₂/D₂ Exchange versus Cyclic Voltammetry

- **Pros**

- Direct measurement of H₂ 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.

