2009 DOE Hydrogen Program Review

Effects of Impurities on Fuel Cell Performance and Durability

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Overview

- **Timeline**
  - Start: Feb. 15, 2007
  - Finish: Feb. 14, 2011
  - Completed: 50%

- **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 FY08
    - CU: $350,000
    - SRNL: $275,000
  - Funding for FY09
    - CU: $337,443
    - SRNL: $200,000

- **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, 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 2008-09**
  - Phenomenological Measurements on FC Components
    - Complete the investigation in detail of CO poisoning of Pt as well as the effect of NH_3 poisoning.
    - Complete the study of NH_3 poisoning of the Nafion® membrane as a function of impurity level, relative humidity, and temperature. Finalize the study of the minimal effect of CO on Nafion® conductivity.
  - Fuel Cell Performance Studies
    - Investigate effect of Cl-containing hydrocarbon (PCE).
    - Carry out long term study of effect of NH_3 poisoning per DOE request.
  - Start correlation of fundamental and FC performance results for NH_3 poisoning.

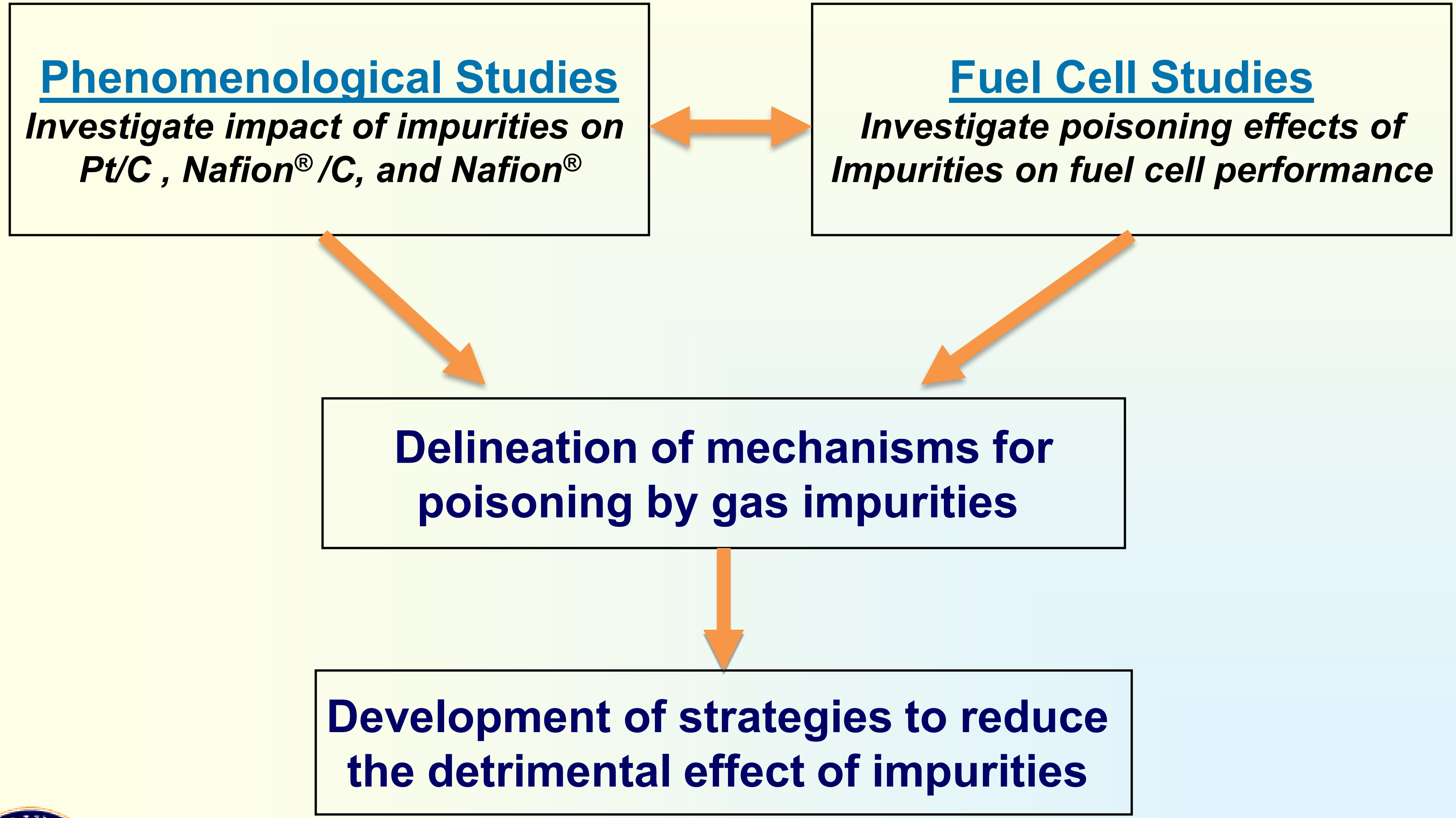
Milestones

🟥 Completed

🟦 Modified

Qtr	Mat. Acquisition /Prep.	Pt/C Study	Nafion® Study	PEMFC Performance 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**:
3		*impact on H_2/D_2 exchange*	*impact on test reaction (HAc est.)*	*consideration of protocol modifications*
4		*impact on H_2-O_2 rxn*	*conductivity*	Effect of **CO**:
5	Prep. of Nafion® membranes	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**:
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 **O_2**:~~ Long Term Study of **NH_3 (DOE)**
10		Effect of **HCOOH**:	Effect of **O_2**:	Effect of **HCOOH**:
11		Effect of **O_2**:	Effect of **HCOOH**:	Effect of **Cl**: **TCE**
12		Effect of **H_2O**:	Effect of **Cl**: **TCE**	Effect of **H_2O**:
13	Prep. of Nafion® membranes	Effect of **Cl_2**: **TCE**	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**:
15		Effect of **He, Ar, N_2**:	Effect of **H_2S**:	Effect of **Impurity Mixtures**
16	**FINAL REPORT**	**FINAL REPORT**	**FINAL REPORT**	**FINAL REPORT**

Technical Approach



Phenomenological 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

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)
- *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


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

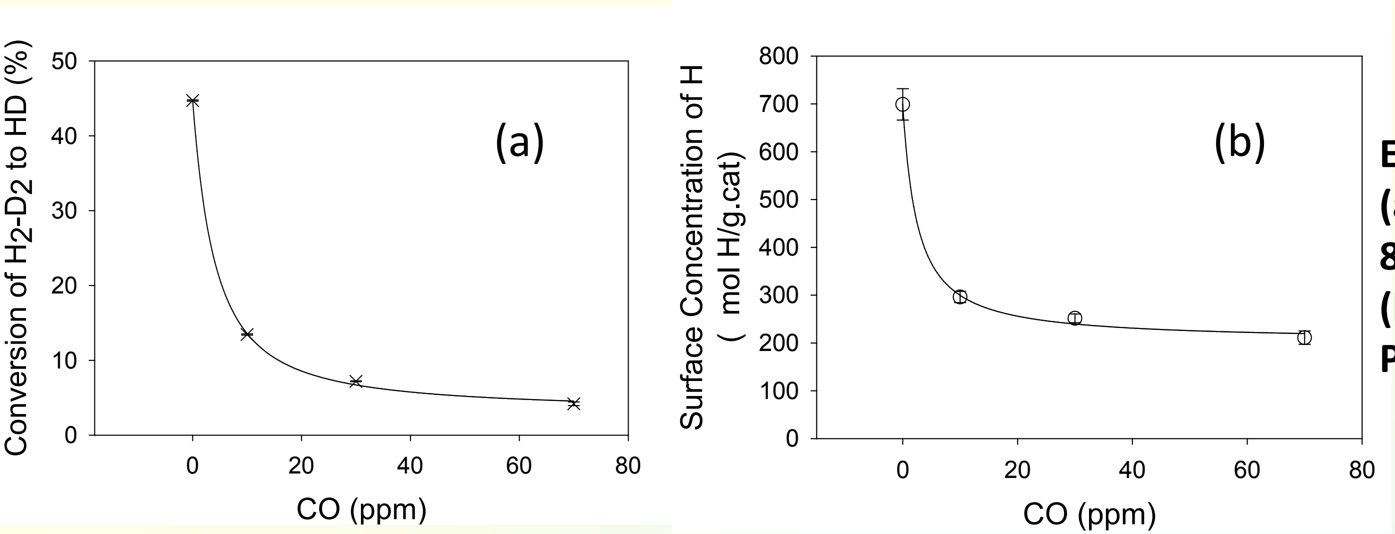
FC Single Cell Test Station

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

Effect of CO on H_2 Activation on Pt/C



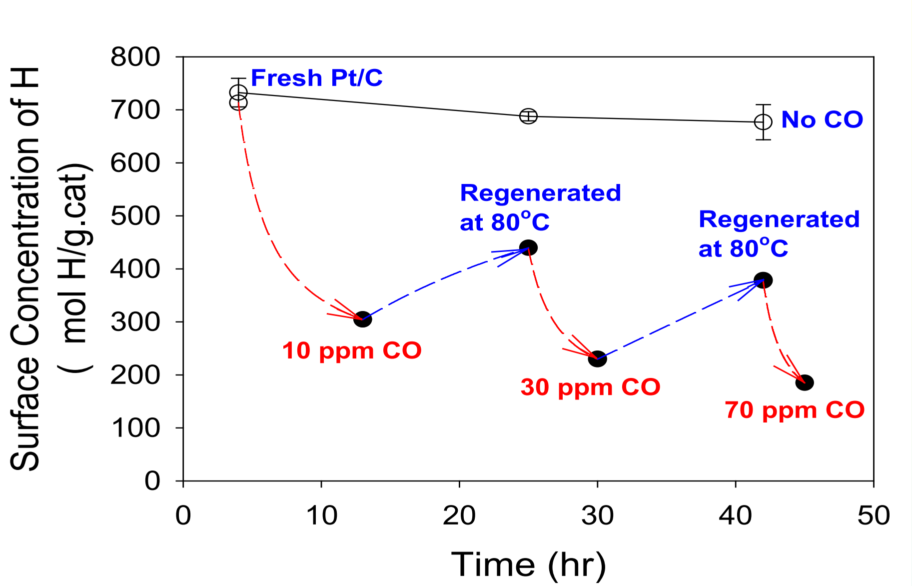
Effect of CO conc. on (a) H_2/D_2 exchange at 80°C and 2 atm and (b) the amount of H on Pt/C .

- **In absence of CO, H_2-D_2 exchange at equilibrium (i.e., H_2 activation very fast).**
- **Significant spillover of H from Pt to C surface. (ca. 230 µmol H spillover/g.cat vs. 370 µmol H on Pt_s/g.cat [H_2 Chem. at RT])**
    - **Static H_2 Chemisorption at 80°C yielded approx. 590 µmol H/g.cat**
- **Presence of 10 ppm CO severely inhibits HD formation by >70% and surface concentration of H by approx. 58%.**
- **These results, in addition to E_a of H_2/D_2 exchange in the presence of CO, seem to indicate that the poisoning effect of CO is a combination of (1) blocking of Pt sites, (2) surface restructuring of Pt in as little as 10^{-9} mbar of CO observed via HP STM (300 – 400K) [Thostrup 2003], and magnified by the (3) structure sensitivity of H_2/D_2 exchange reaction [Somorjai 1986]**

Thostrup P., E.K. Vestergaard, T. An, E. Lægsgaard, F. Besenbacher, *J. Chem. Phys.* 118 (2003) 3724.
Somorjai G.A. and J. Carrazza, *Ind. Eng. Chem. Fundam.* 25 (1986) 63.

Technical Accomplishments and Progress

Regeneration of Pt/C After Exposure to CO



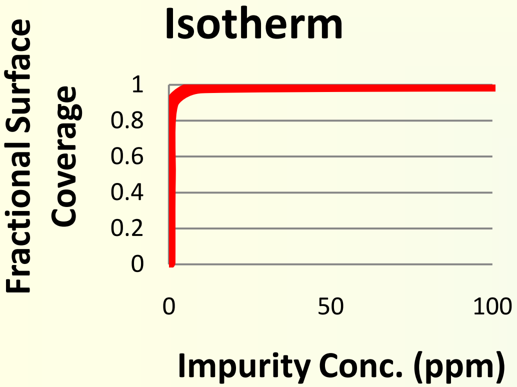
Surf. conc. of ads. H on Pt/C with and w/o CO exposure. (Pt/C was treated with flowing H_2 overnight at 80°C after exposure to 10 ppm CO and 30 ppm CO.)

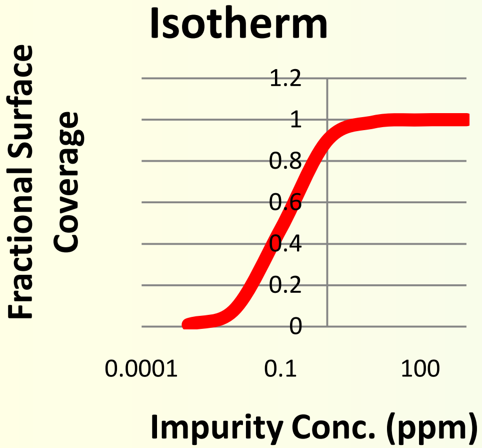
- **Severe loss in H ads. unable to be sig. recovered even after overnight (12h) exposure at 80°C to flowing H_2, indicating very slow recovery of CO poisoned Pt sites in pure H_2.**
- **After exposure to 10 ppm CO, overnight recovery from 305 to 440 μmoles H/g Pt/C, vs. 688 for surface never exp. to CO.**
- **Comparison to PEMFC data [Jimenez et al., 2005] seems to indicate that even though pulsing of CO increased CO tolerance of their Pt-electrode, the poisoning effect of CO is still cumulative and the benefit of pulsing would diminish over time.**

Jimenez, S., J. Soler, R.X. Valenzuela, L. Daza, *J. Power Sources* 151 (**2005**) 69-73.

Technical Accomplishments and Progress

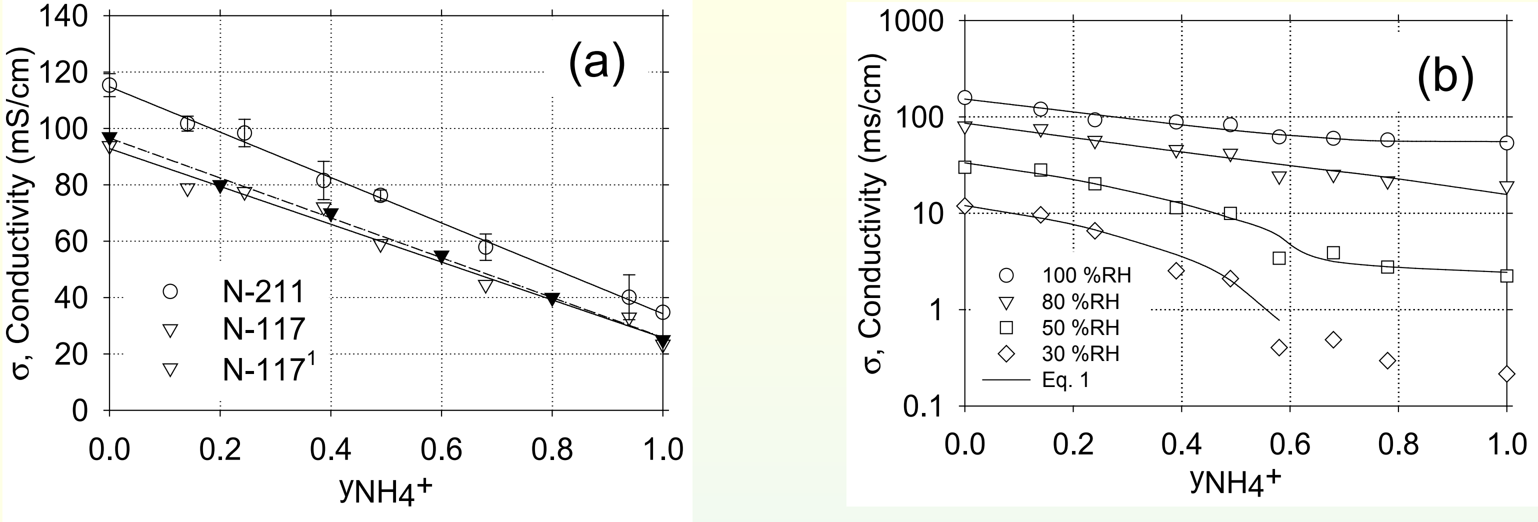
Impurity Coverage of Pt





- For impurities like CO with a large equilibrium ads. constant for Pt, the near complete coverage of Pt occurs at very low concentrations of the impurity.
- Because of H spillover, the “H coverage” of Pt cannot be determined directly.
- We are working towards determination of $\theta_{impurity}$ directly and θ_H indirectly. An isotherm for the impurity on Pt will be able to be constructed.
- CO coverage of Pt should be able to be determined by TPD even for low concentrations. That for other poisons for Pt (such as PCE) will also be determined using appropriate methods.
- The time to reach state-state coverage of the impurity on the Pt catalyst in a PEM fuel cell is a function of:
  - impurity concentration in the fuel
  - flow rate of the fuel
  - Pt loading of the catalyst
  - competition for ads. from other gas species
  - adsorption equilibrium
  - O_2 bleed through to the anode

Effect of NH_4^+ ion conc. on the conductivity of Nafion®



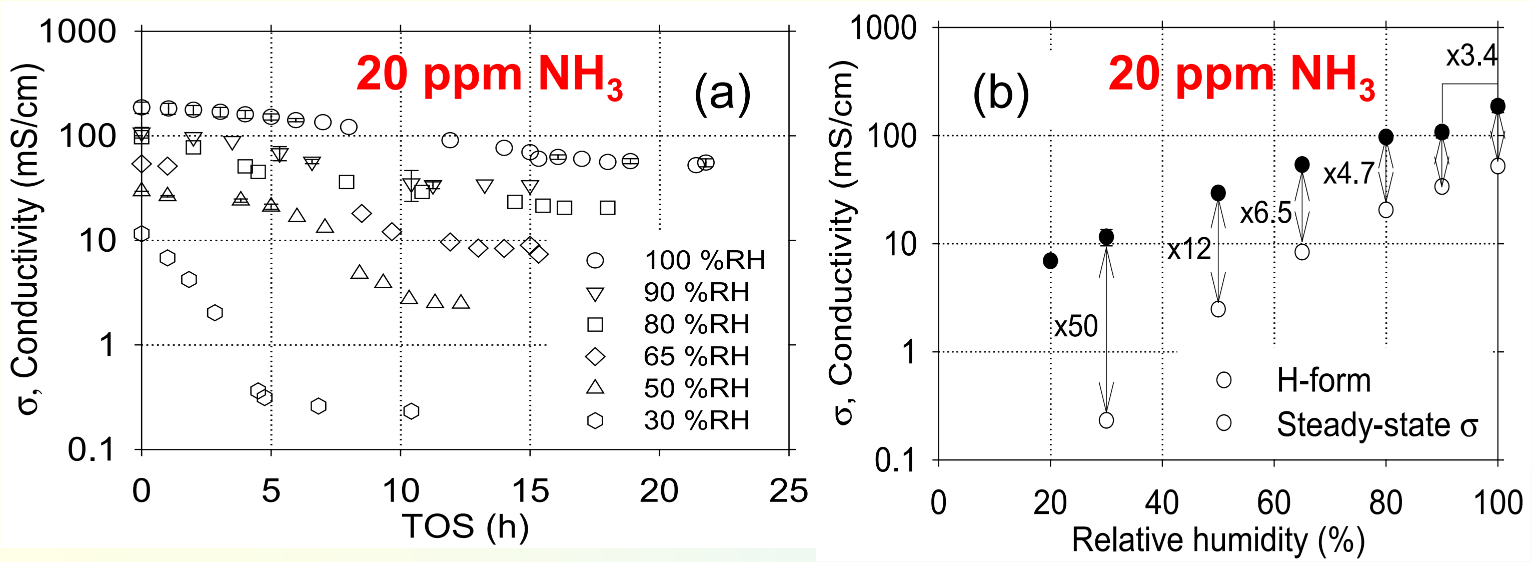
Conductivity of N-211 (a) at RT in deionized H_2O; (b) at 80°C in He.

- The conductivity in deionized water decreases linearly with an increase in y_{NH4+}, the NH_4^+ content in a membrane.
- The conductivity in the vapor-phase is a more dramatic function of y_{NH4+} .
    - %RH has a significant effect on the decrease in conductivity with NH_4^+ content.
    - NH_3 poisoning is less serious at higher RHs.
- Previous efforts[2,3] to predict FC performance used conductivity measured in liquid electrolyte. Conductivity meas. in the vapor phase at a particular humidity would provide a better result.

Note. N-211s were prepared by immersion in HCl solutions containing known amount of NH_4^+ ions .

*(1) R. Halseid et al., J. Electrochem. Soc., **151**, A381 (2004),*
*(2) Kienitz et al., Electrochimica Acta **54,** 1671 (2009),*
*(3) R. Halseid et al., J. Power Sources, **154**, 343 (2006).*

Effect of humidity on the real time conductivity of Nafion® membrane

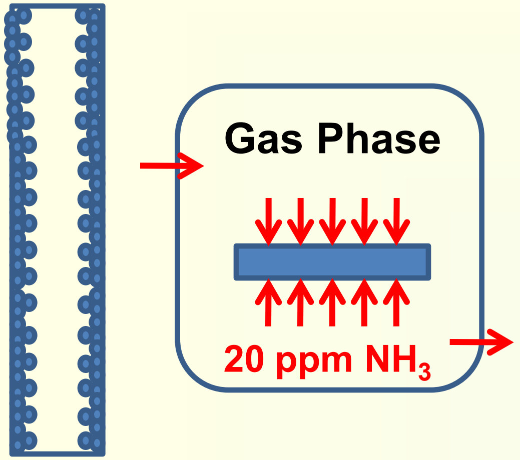


Ionic conductivity of N-211 (30-100% RH, 80°C) in the presence of 20 ppm NH_3 as a function of (a) time-on-stream (TOS); (b) relative humidity.

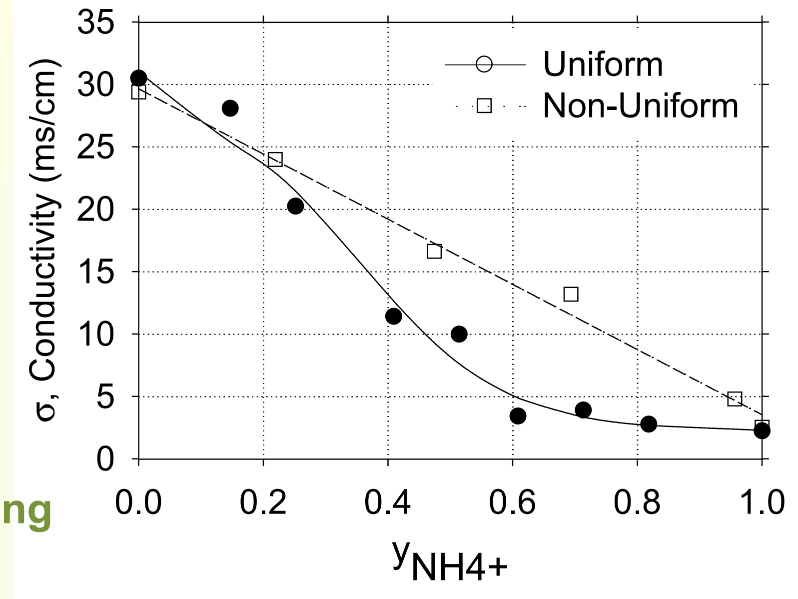
- **NH_4^+ poisons much slower at higher %RH, even for the same NH_3 conc.**
- **This slower poisoning is probably due to the competitive adsorption between H_2O and NH_3 and possibly mass transport limitations.**
- **The impact of ammonia poisoning on conductivity is more severe at low humidity than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

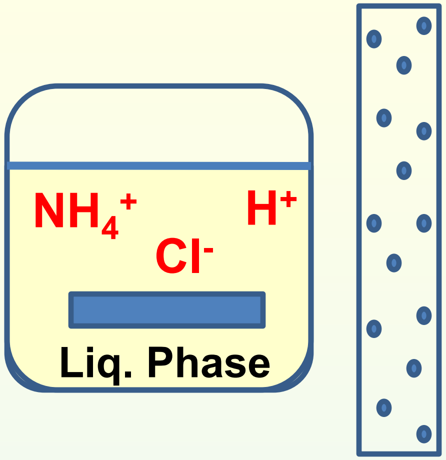
Technical Accomplishments and Progress

Effect of NH_4^+ distribution on the conductivity of the Nafion® membrane



Non-Uniform NH_3 poisoning





Uniform NH_4^+ poisoning

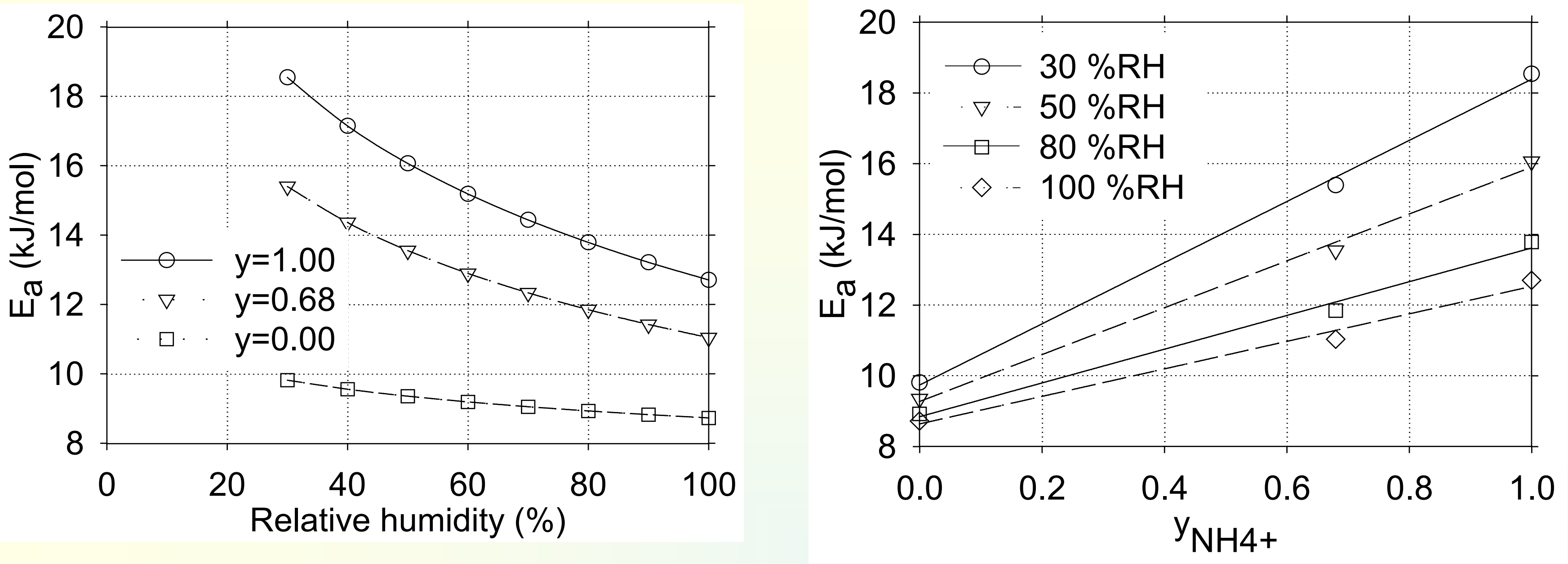
Conductivity at 50%RH, 80°C for non-uniform and uniform NH_3 poisoning of N-211.

- **The distribution of NH_4^+ in N-211 affects the conductivity.**
- **With non-uniform NH_3 poisoning, the conductivity has a linear relationship with y_{NH4}^+ (a combination of pure H^+ cond. and NH_4^+ cond.).**
- **With uniform NH_4^+ poisoning, the conductivity decreases more dramatically with an increase in y_{NH4+} since proton transport via the Grotthuss mechanism is significantly inhibited, in agreement with Saito et al.***

* *Saito et al., J. Phys. Chem. B 2005, 109, 3112-3119*

Technical Accomplishments and Progress

Effect of NH_4^+ ions on the E_a of the ionic conductivity



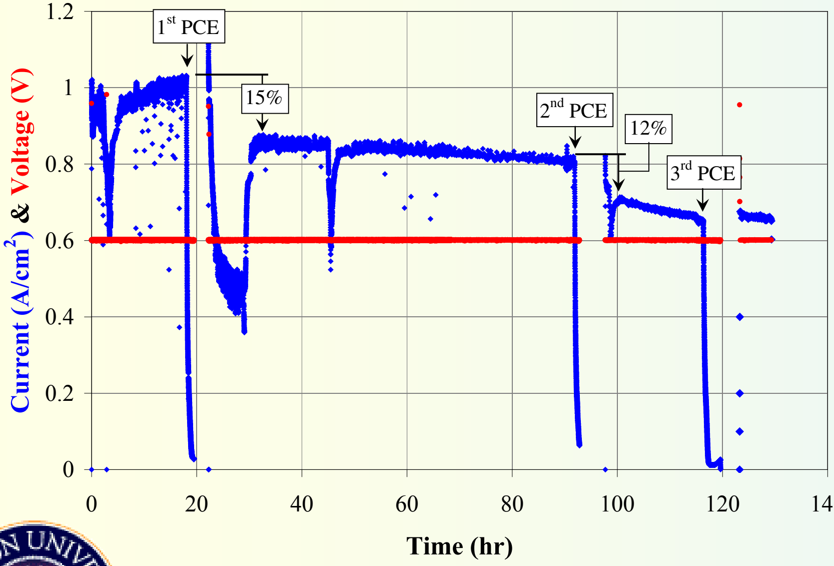
E_a of the conductivity of N-211 as a function of (a) relative humidity; (b) y_{NH4+}.

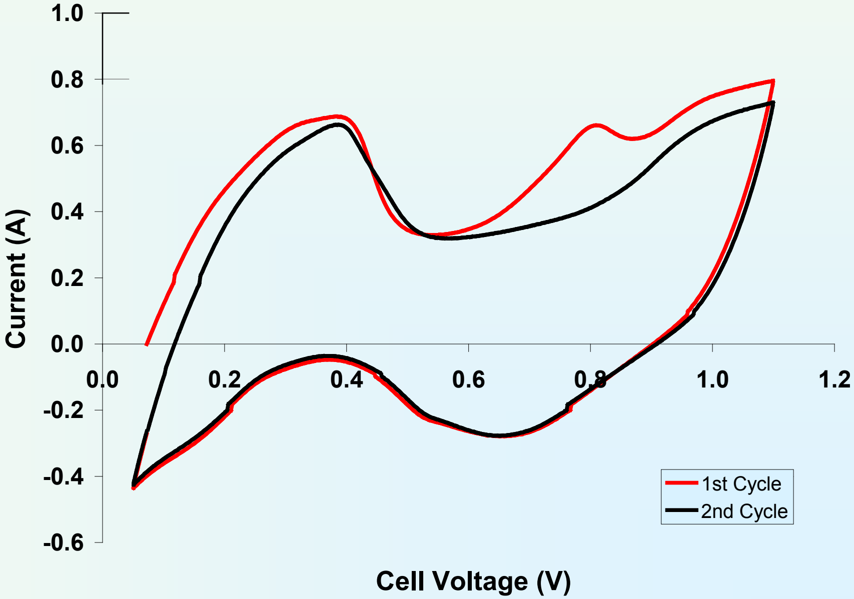
- The activation energy of conductivity decreases as the humidity increases for all NH_4^+ concentrations.
- E_a is a strong function of the NH_4^+ content of the membrane.
- One can predict the conductivity of Nafion® membranes containing different amounts of NH_4^+ ions at any humidity and temperature (60 – 90°C).

Technical Accomplishments and Progress

PCE Cyclic Voltammagram Cleaning

- Multiple poisoning runs were performed at 30 ppm PCE to see recovery behavior.
- Anode (N_2/H_2) Cyclic Voltammagrams were performed after each poisoning.
- Oxidation peak was centered at 0.8 V. Wide peak may indicate multiple oxidation mechanisms.
- Ca. 85% of performance recovered after CV for first 2 poisoning cycles.
- Irreversible poisoning complete after 2 cycles at 30 ppm.

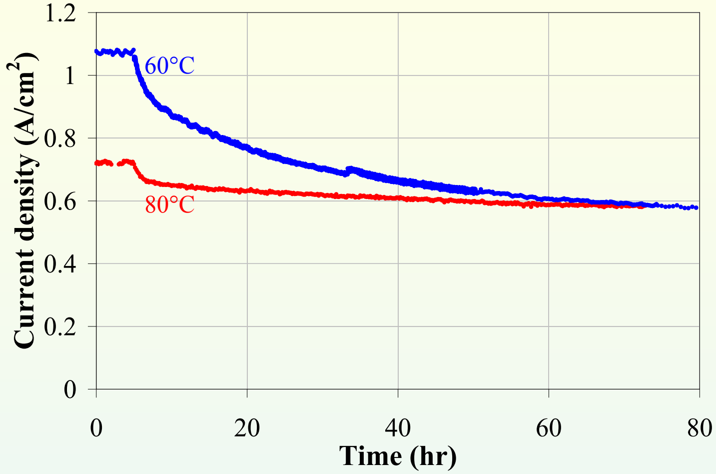


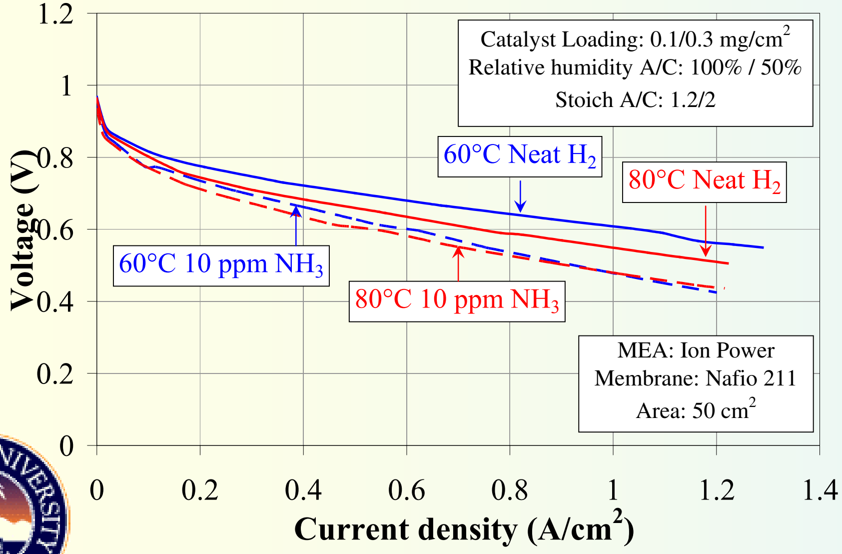


Technical Accomplishments and Progress

10 ppm NH_3 Poisoning Polarization

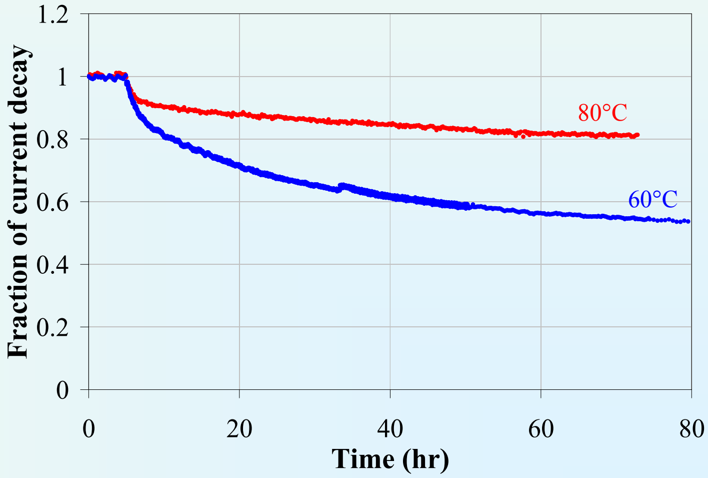
- Tests used ISO matrix – 1100 EW, 25 mm membrane, %RH- 100/50 (A/C).
- 60°C and 80°C show equivalent polarization during 10 ppm NH_3 poisoning.
- Larger change in polarization from steady state occurred at 60°C.
- Poisoning kinetics are slower at 60°C, but with faster initial poisoning rate at 80°C.
- First segment shows poisoning of fresh MEA.
- Current decay characterized as a fraction of the initial steady state current for both temperatures.





Catalyst Loading: 0.1/0.3 mg/cm^2
Relative humidity A/C: 100% / 50%
Stoich A/C: 1.2/2

MEA: Ion Power
Membrane: Nafio 211
Area: 50 cm^2

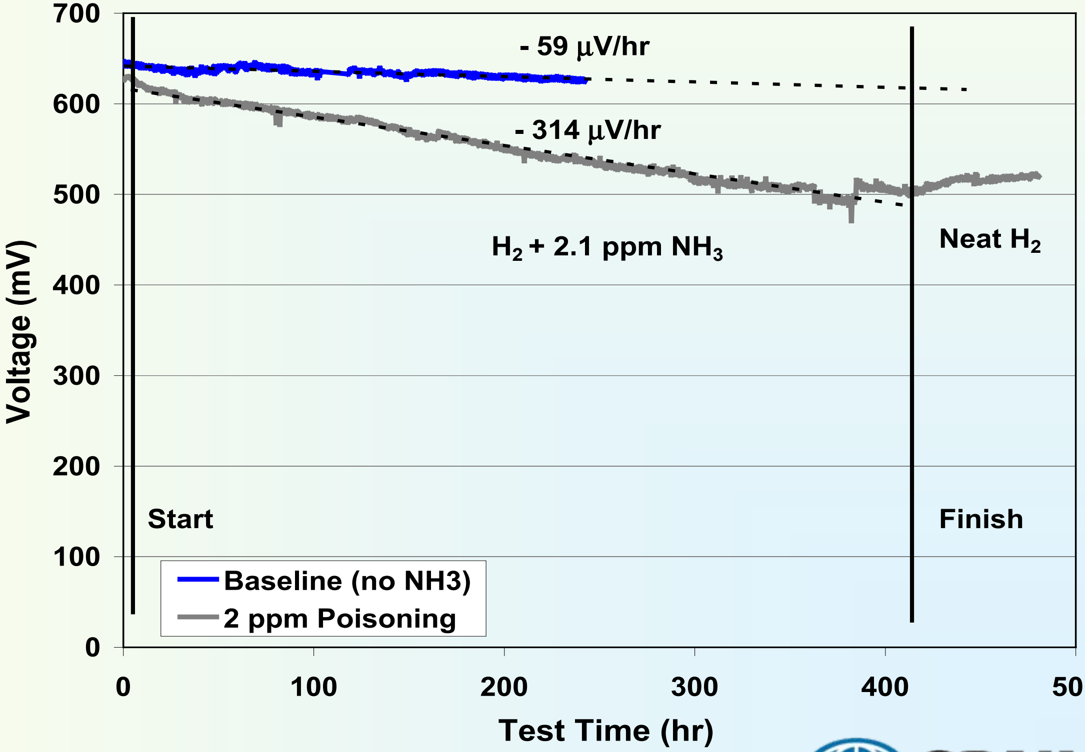


Technical Accomplishments and Progress

2 ppm NH_3 Poisoning Kinetics

- NH_3 poisoning was nearly linear with time. Degradation rate was 5 times the baseline degradation.
- Contrary to 10 ppm tests, minimal performance recovery was observed during 50 hours in neat hydrogen.
- Anode and cathode CVs after run showed no residual NH_3 adsorption on catalyst.

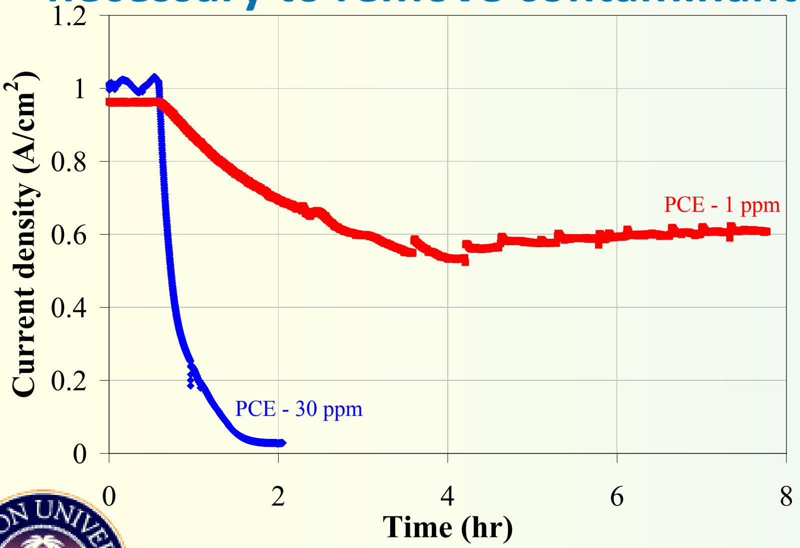
- ➢ MEA – Ion Power
- ➢ Membrane – Nafion® 211
- ➢ %RH- 100/100 (A/C)
- ➢ Pt Catalyst Loading – 0.3/0.3 mg/cm^2
- ➢ Stoich – 1.2/2.0
- ➢ Active Area – 50 cm^2

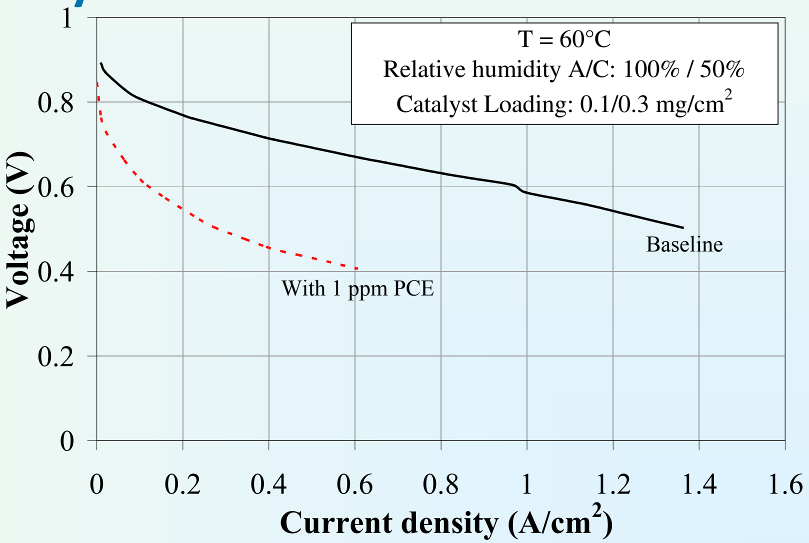


Technical Accomplishments and Progress

Perchloroethylene (PCE) Poisoning

- PCE is a model chlorinated hydrocarbon used as a cleaning agent.
- At 1 ppm, 60°C and 0.6 V, PCE degrades cell current by 40% in 4 hours.
- After poisoning, there is only minimal recovery in neat hydrogen.
- CVs suggest PCE is an anode catalyst poison that can be electrochemically oxidized at 0.8 V.
- There is no effect on membrane conductivity as measured by impedance.
- Data on subsequent runs suggest that extensive system purging may be necessary to remove contaminant from system.





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 (2009-2010)

- **Activities**
  - Complete studies of the effect of CO in presence of water vapor on H_2 activation on Pt/C.
  - Study the effects of PCE, CO_2, ethane, and ethylene on fundamental processes (on Pt & Nafion® components) and fuel cell performance to understand poisoning mechanisms and rates.
  - Perform EIS experiments to characterize membrane and ionomer conductivity during NH_3 poisoning in FC.
  - As requested by DOE, test fuel cell performance with 0.1 ppm NH_3 at 60°C and 80°C and 50% anode RH for 1000 hours.
  - Work with DOE H_2 Fuel Quality Working Group to Support ISO Standard Process
  - Use advanced online spectroscopic techniques to characterize NH_3 transport in the fuel cells.
  - Provide Argonne Nat. Lab Modeling Group with phenomenological data on NH_3 poisoning of Nafion® and CO poisoning of Pt.
- **Upcoming Milestones**
  - Complete phenomenological studies of effects of CO, NH_3, and PCE on Pt/C, Nafion®-Pt/C, Nafion®/C, and Nafion® membrane.
  - Undertake phenomenological studies of effects of CO_2, acetaldehyde, and ethylene on Pt, Nafion®/C, and Nafion® membrane.
  - Complete FC runs of effects of CO, NH_3 , CO_2, PCE and acetaldehyde on FC performance.
- **Decision Points** None

Summary

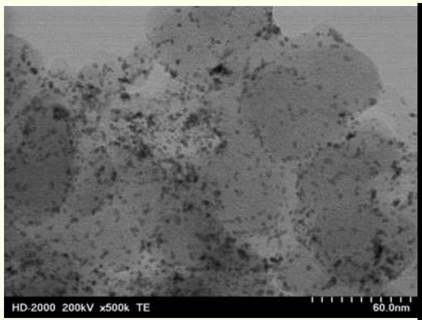
- There is significant H spillover from Pt to the carbon support at FC conditions (≈H coverage of Pt).
- CO significantly decreases H_2 activation, H chemisorption, and H spillover on Pt/C.
- Neither CO nor perchloroethylene (PCE) have any significant effect on the conductivity of Nafion®.
- However, 1 ppm PCE in the H_2 fuel decreases fuel cell current by 40% at 0.6 V in less than 4 hours.
- NH_3 does not have an effect on H_2 activation on Pt.
- The effect of NH_3 on the conductivity of Nafion® is a strong function of relative humidity, with a reduction in conductivity of 3.4X at 100% RH, but 50X at 30% RH. Poisoning also occurs at a slower rate at higher %RH.
- NH_3 poisoning at 80°C causes significantly less decrease in fuel cell performance than at 60°C, but poisoning kinetics are faster.
- NH_3 shows a significant effect on fuel cell performance at 2 ppm. Testing will be conducted to determine effects at 0.1 ppm at 60°C and 80°C.
- SRNL is using a permeation tube impurity generator to facilitate testing at DOE ISO hydrogen quality standard limits.

Supplemental Slides

Experimental: Materials*

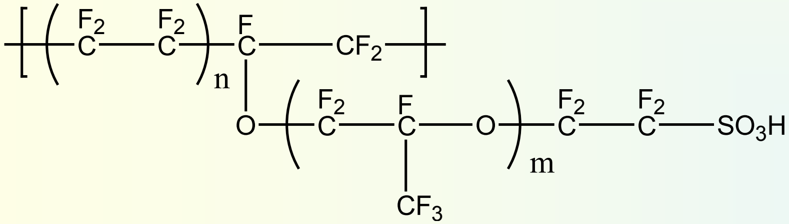
- **Anode: 20 wt% Pt/C (E-TEK)**
  - **Pt Particle Size: 22 Å (Co.)**
  - **BET Surface Area: 128 m²/g (Co.)**
- **Cathode: 40 wt% Pt/C (E-TEK)**
  - ***Pt Particle Size: 29 Å (Co.)**
  - ***BET Surface Area: 100 m²/g (Co.)**

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)**



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

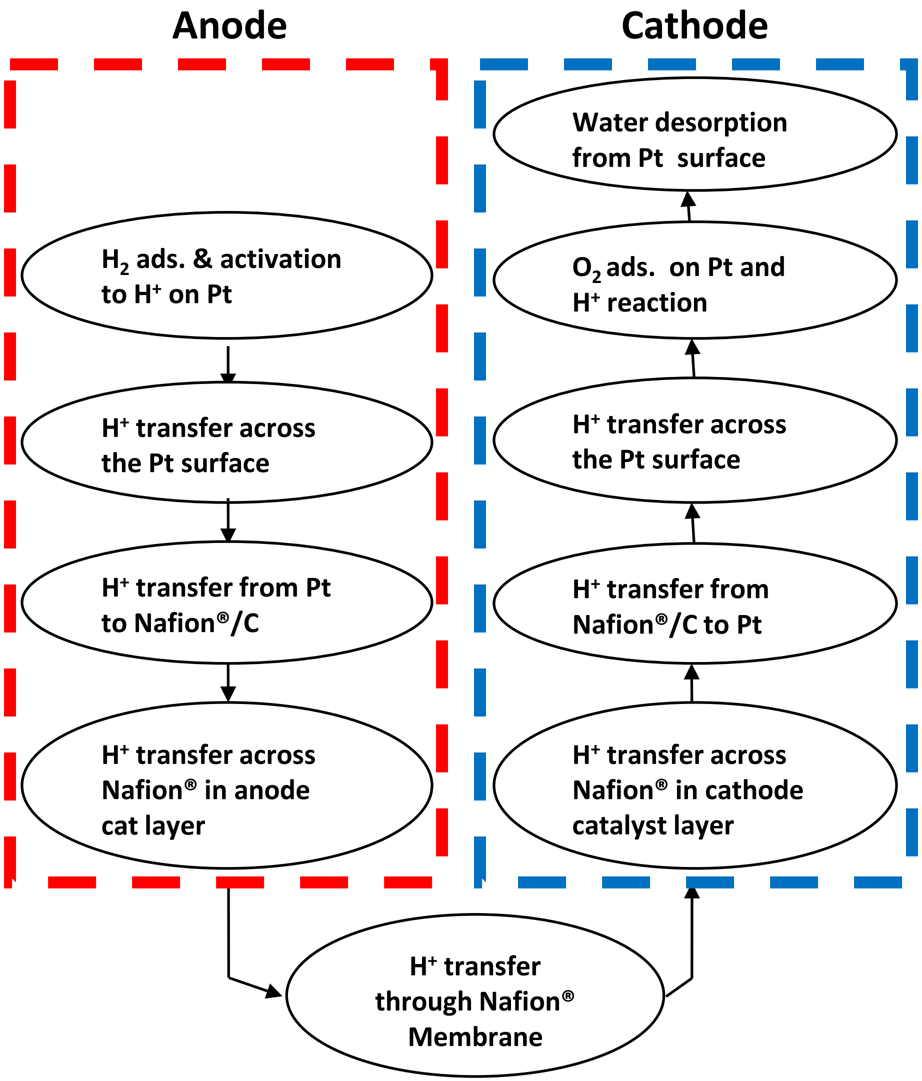
Acid Site Density:

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

- **Carbon Black Powder (XC-72R)**
  - **BET Surface Area: 250 m²/g (Co.)**
- **MEAs (Ion Power)**
- **Nafion® 212 Membrane EW 1100 (DuPont)**

* *Commercial Products*

Rate Steps during FC Operation



Anode

Cathode

H_2 ads. & activation to H^+ on Pt

H^+ transfer across the Pt surface

H^+ transfer from Pt to Nafion®/C

H^+ transfer across Nafion® in anode cat layer

H^+ transfer through Nafion® Membrane

H^+ transfer across Nafion® in cathode catalyst layer

H^+ transfer from Nafion®/C to Pt

H^+ transfer across the Pt surface

O_2 ads. on Pt and H^+ reaction

Water desorption from Pt surface

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

Clemson/SRNL NH_3 Collaboration

Clemson

- Fundamental characterization of NH_3 poisoning on ionomer
- Measurements of NH_3 and %RH effects on conductivity of Nafion® 211
- Understanding of conductivity as a function of NH_4^+ exchange fraction
- Characterization of sulfonic acid site poisoning rates

SRNL

- *In-situ* NH_3 poisoning tests of Nafion® 211 based MEA
- NH_3 testing down to ISO fuel quality standard level
- Impedance measurements of poisoned MEAs
- Separation of conductivity of membrane and of catalyst layer ionomer using EIS

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 takes place much faster and more uniformly than in a FC

H_2/D_2 Exchange Mechanism

- H_2-D_2 exchange [300 < T (K) < 500]
  - Bonhoeffer-Farkas mechanism*

    (S denotes an active catalyst site)

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

  - 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 H_2 and D_2

    (Tafel reaction) (i.e., H_2 activation)

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

Kinetics of H_2 Exchange and Electro-oxidation*

- Assuming H_2 dissociation step being rate determining in **H_2/D_2 exchange**:

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

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 H_2**:
  - Volmer reaction is the charge transfer step

$$2\mathrm{M} + \mathrm{H_2} \rightleftarrows 2\mathrm{HM}$$

$$2\mathrm{HM} \rightleftarrows 2\mathrm{M} + 2\mathrm{H}^+ + 2\mathrm{e}^-$$

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

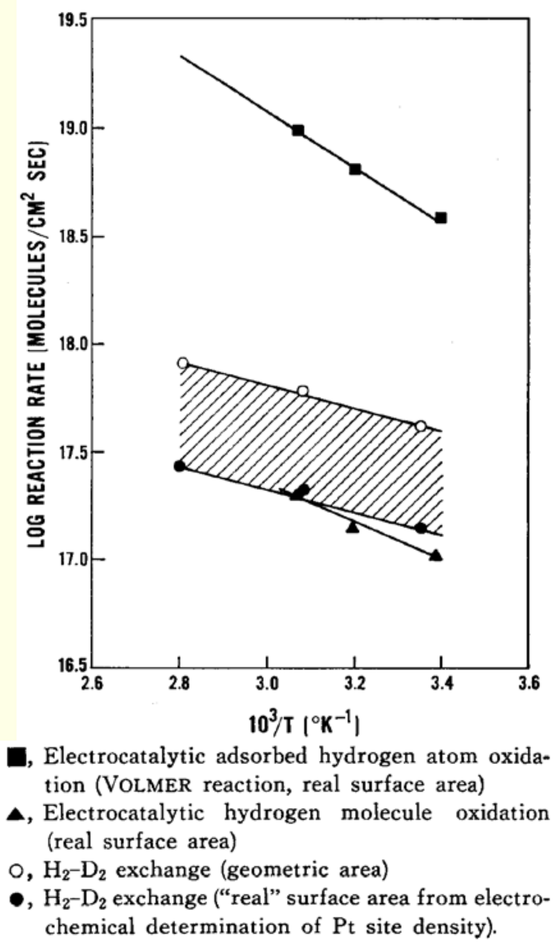
$$i_{\mathrm{A}} = nFk_{\mathrm{at}} C_{\mathrm{H_2}} (1-\theta)^2 - nFk_{\mathrm{ct}} \theta^2$$

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**

*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



■, Electrocatalytic adsorbed hydrogen atom oxidation (VOLMER reaction, real surface area)

▲, Electrocatalytic hydrogen molecule oxidation (real surface area)

○, H_2–D_2 exchange (geometric area)

●, H_2–D_2 exchange ("real" surface area from electrochemical determination of Pt site density).

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

Technical Accomplishments and Progress

Apparent E_a of H_2/D_2 Exchange in the Absence/Presence of CO

Table 1. Apparent activation energies of H_2-D_2 exchange Pt/C with varying concentrations of CO at T = 80°C, P = 2 atm. Average E_a is 19.5 ± 1.33 kcal/mol.

CO (ppm)	E_a (kcal/mol)
0	4.5[a], 5.3[b]
10	20.6
20	18.0
40	19.8
*	17.4[c]

*200 mTorr H_2, 20 mTorr D_2, and 5 mTorr CO

- **Due to being reaction equilibrium limited, measurements of E_a for H_2/D_2 exchange in the absence of CO have only been successful via molecular beam studies at very low pressure.**
- **The increase in E_a upon CO poisoning seen by us is indicative of perhaps a restructuring of Pt surfaces by CO [[c]Thostrup 2003] or a change in rate-determining step [Montano 2006], but also likely is a contribution of $\Delta H_{ads,\,CO}$ to apparent E_a.**

[a] Bernasek S.L. and G.A. Somorjai, *J. Chem. Phys.* 62 (1975) 3149.

[b] Montano M., K. Bratlie, M. Salmeron, G.A. Somorjai, *J. Am. Chem. Soc.* 198 (2006) 13229.

[c] Thostrup P., E.K. Vestergaard, T. An, E. Lægsgaard, F. Besenbacher, *J. Chem. Phys.* 118 (2003) 3724.

Technical Accomplishments and Progress

Surface Concentration of Pt from H_2/CO Chemisorption

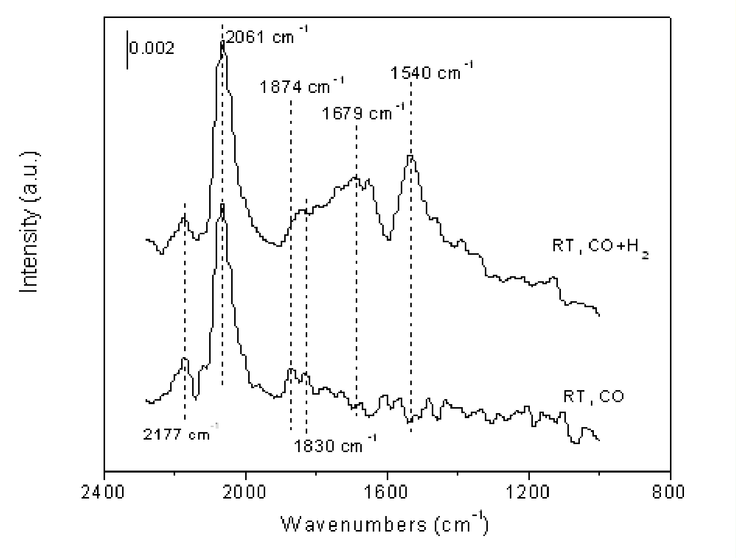


Figure 3. DRIFTS spectra of CO ads. on 20 wt% Pt/C (from 4% CO/H_2 and 100% CO at RT.

Table 2. Est. of Pt Surf. conc. from H_2 or CO chemis.

Adsorption Gas	Pretreatment Condition	Analysis Temp. (°C)	Amount of CO/H Adsorbed (µmol/g)
CO	80°C for 3hrs	35	260
	80°C for 3hrs	80	280
H_2	80°C for 3hrs	35	370
	80°C for 3hrs	80	590

- **Linear CO (CO:Pt = 1:1): 2061 cm^{-1} and bridged CO (CO:Pt = 1:2): 1874-1830 cm^{-1}**
- **Comparison of linear and bridge-bonded CO show a ratio of 10:1.**
- **Pt surface concentration is est. to be 290 µmol Pt_s/g.cat (calculated from CO chemisorption at 35°C).**
- **Compared to CO results at 80°C, H_2 chemisorption indicated significant spillover of H, even at 35°C but especially at 80°C.**

Technical Accomplishments and Progress

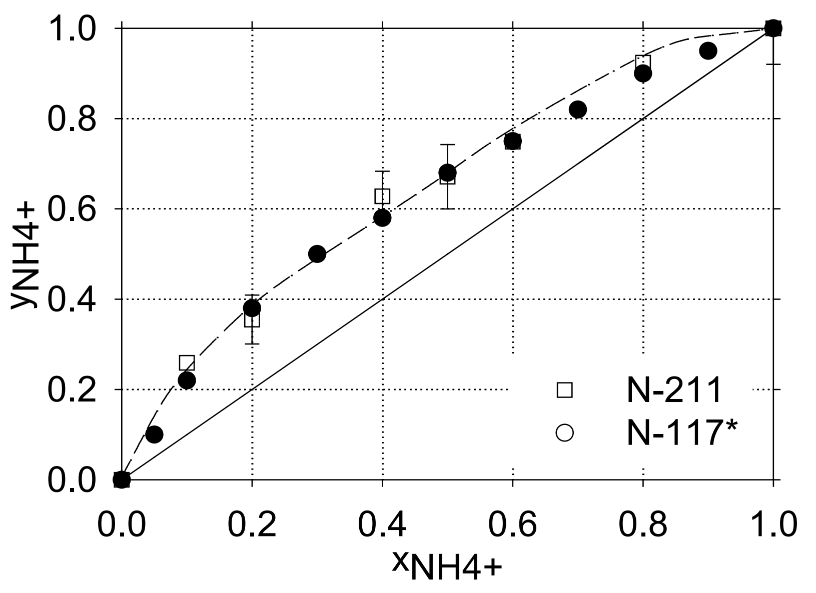
H_2/CO Chemisorption Results

Adsorption Gas	Pretreatment Condition	Analysis Temp. (°C)	Equilibration Interval (sec)	Amount of CO/H Adsorbed (µmol/g)	Metal Dispersion (%)	Avg. Pt Particle Size (nm)[a]
CO	350°C for 12hrs[b]	35	10	270	27	4.07
	350°C for 2hrs	35	150	300	30	3.67
	80°C for 3hrs	35	20	260	26	4.17
	80°C for 3hrs	80	20	280	28	3.96
H_2	350°C for 12hrs[b]	35	10	670	67	1.65
	350°C for 2hrs	35	200	620	62	1.76
	80°C for 3hrs	35	200	680	68	1.62
	80°C for 3hrs	35	20	370	37	2.94
	80°C for 3hrs	80	20	590	59	1.86

Results for H_2/CO chemisorption on 20 wt% Pt/C with various pretreatment conditions, analysis temperatures, and equilibration intervals (used to determine equilibrium point).

Technical Accomplishments and Progress

Equilibrium relationship of NH_4^+ uptake in Nafion® membranes



Equilibrium of NH_4^+ in liquid phase and membrane.

Where x_{NH4+} is the fraction of ammonium ions in a 0.1 M Cl^- aqueous solution and y_{NH4+} is the ammonium composition in the membrane.

- **The experimental result suggests that NH_4^+ has a slightly higher affinity than H^+ for the sulfonic groups in Nafion® membranes.**
- **The experimental results for N-211 are in agreement with Halseid et al.* who studied the equilibrium ammonium uptake of N-117.**

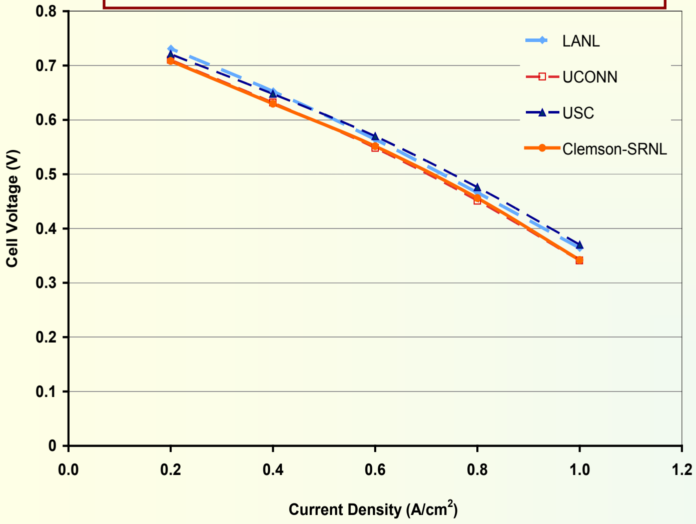
* *R. Halseid et al., J. Electrochem. Soc.,* ***151****, A381 (2004)*

Additional Slides

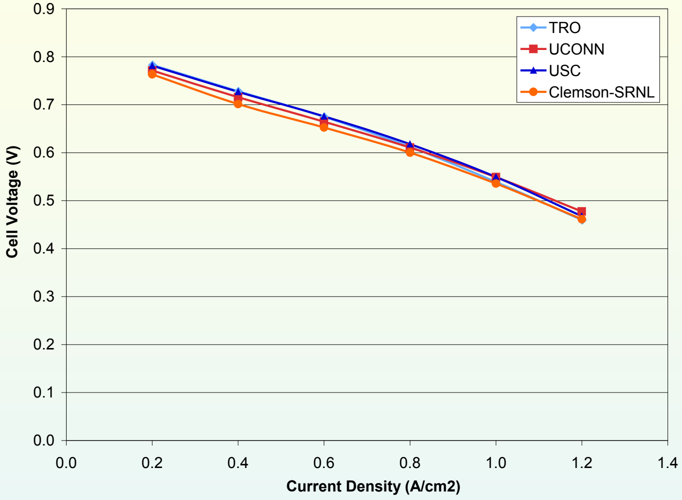
Previous Results

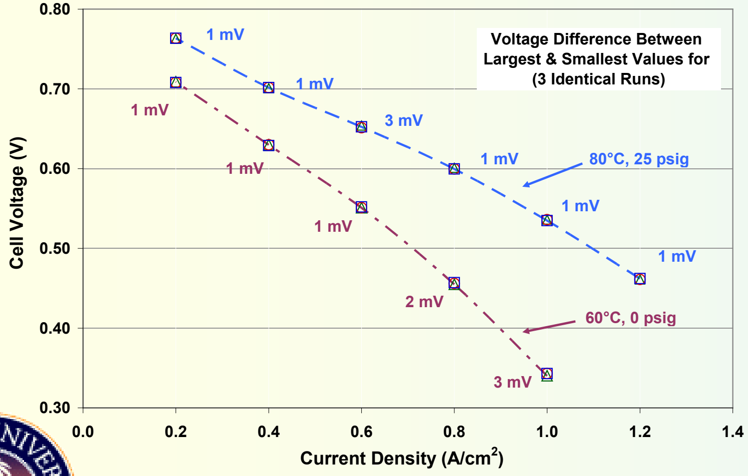
USFCC Round Robin: *SRNL FC Results*

60^{o}C, 0 psig, 100% RH



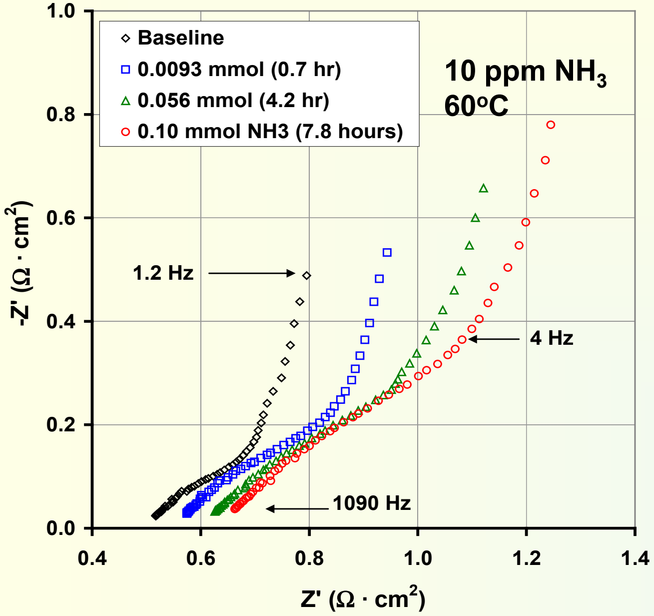
80^{o}C, 25 psig, 100% RH

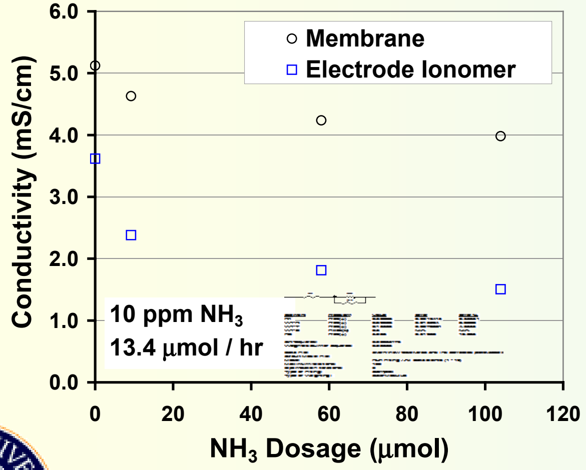




- ☐ Excellent reproducibility was found between labs and FC test stations.
- ☐ Reproducibility of the SRNL FC test station was excellent.

Electrochemical Impedance Spectroscopy (EIS):
10 ppm NH_3 Effect on Membrane & Ionomer @ 60°C



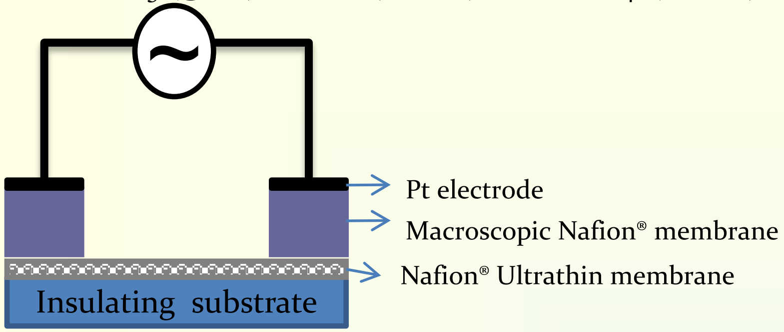


- The baseline run before poisoning is shown in black.
- Area corrected membrane resistance is given by the high frequency intercept with the x-axis.
- The ionomer resistance is proportional to the length of the "45°" line segment between 1090 Hz and ca. 4 Hz.
- This analysis method shows that both the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

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)

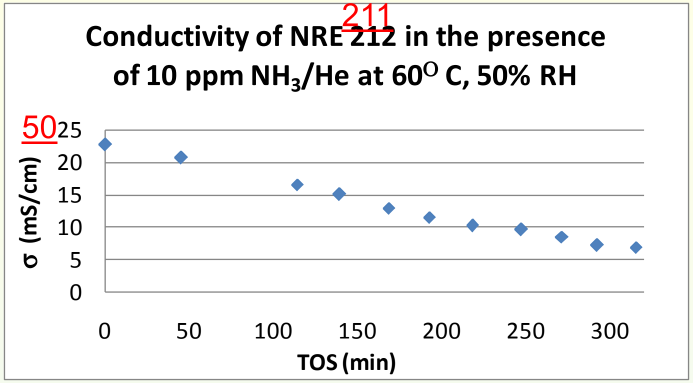
Impedance Measurement: *10 ppm NH_3 on Nafion® 211*

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

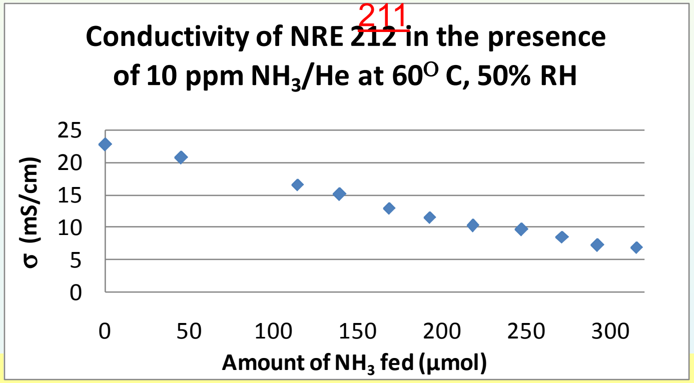


Conditions: T = 60-80°C, RH =0-100%, 0- 100 ppm NH_3 in He

- **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.**



Conductivity of NRE ~~212~~ 211 in the presence of 10 ppm NH_3/He at 60° C, 50% RH



Conductivity of NRE ~~212~~ 211 in the presence of 10 ppm NH_3/He at 60° C, 50% RH

☐ **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).****

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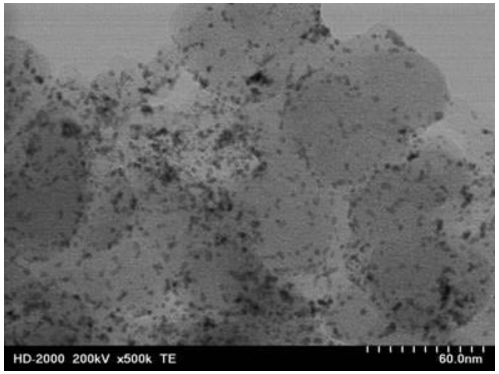
* *T.E. Springer, J. Electrochem. Soc., 138, 2334 (1991).*

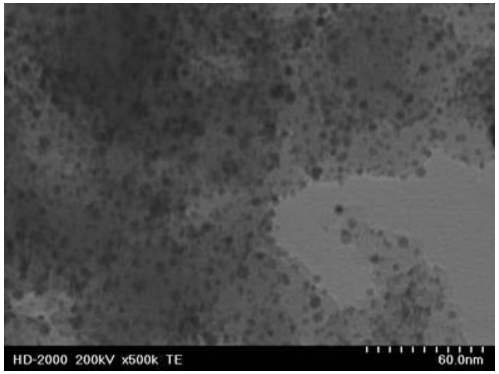
** *F.A. Uribe, T.A. Zawodzinski Jr., S. Gottesfeld, J. Electrochem. Soc. 149 (2002) A293.*

20 wt% Pt/C

- **BET Surface Area: 128 m^2/g**
- **TEM:**

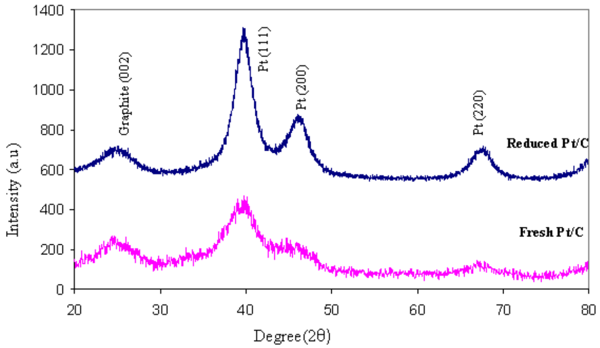


Fresh Pt/C



Reduced Pt/C

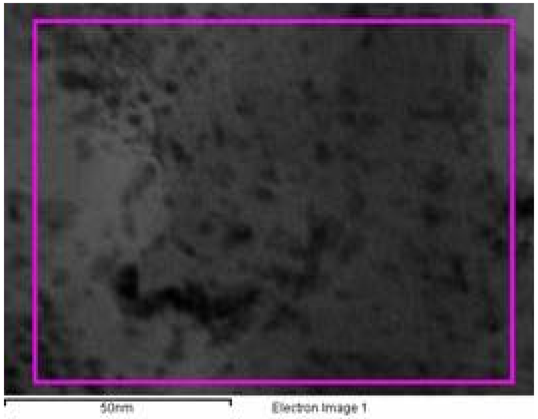
- **XRD:**

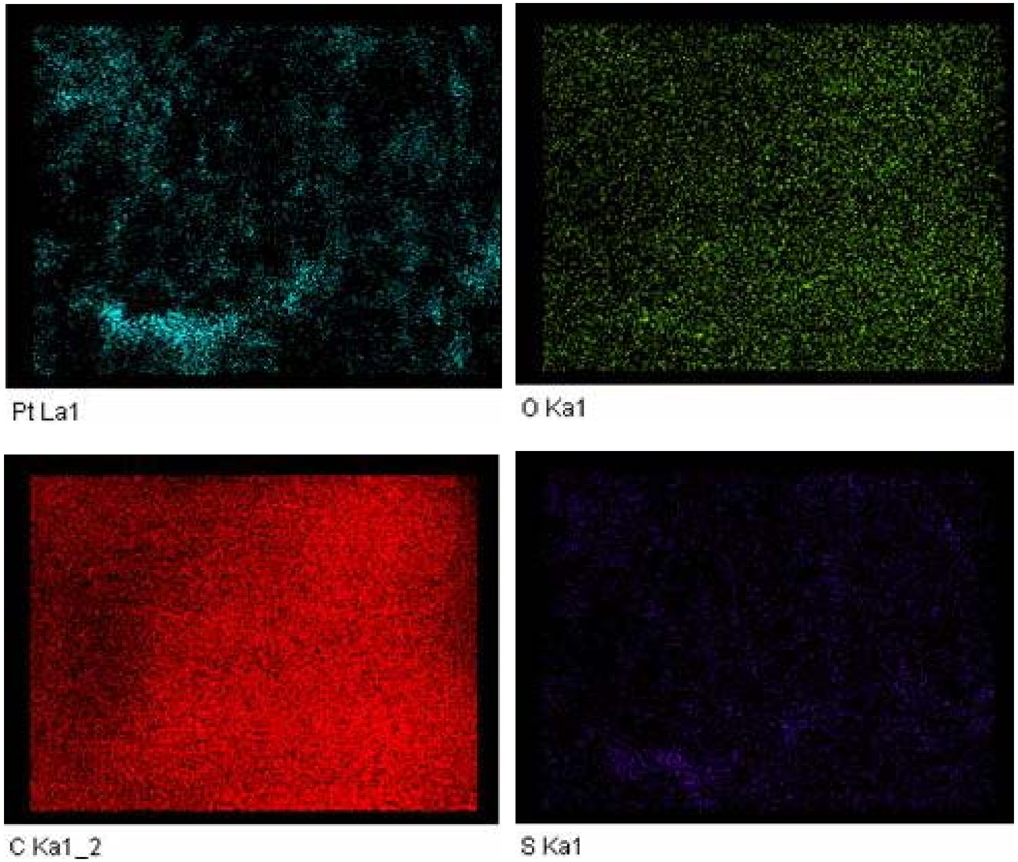


- **On the fresh Pt/C catalyst, the Pt particles are highly dispersed (avg. Pt particle size ca. 2.9 nm).**
- **During reduction, some aggregation of the Pt particles occurs (avg. Pt particle size ca. 4.8 nm).**

20 wt% Pt/C

- **TEM & EDS - Fresh Pt/C:**

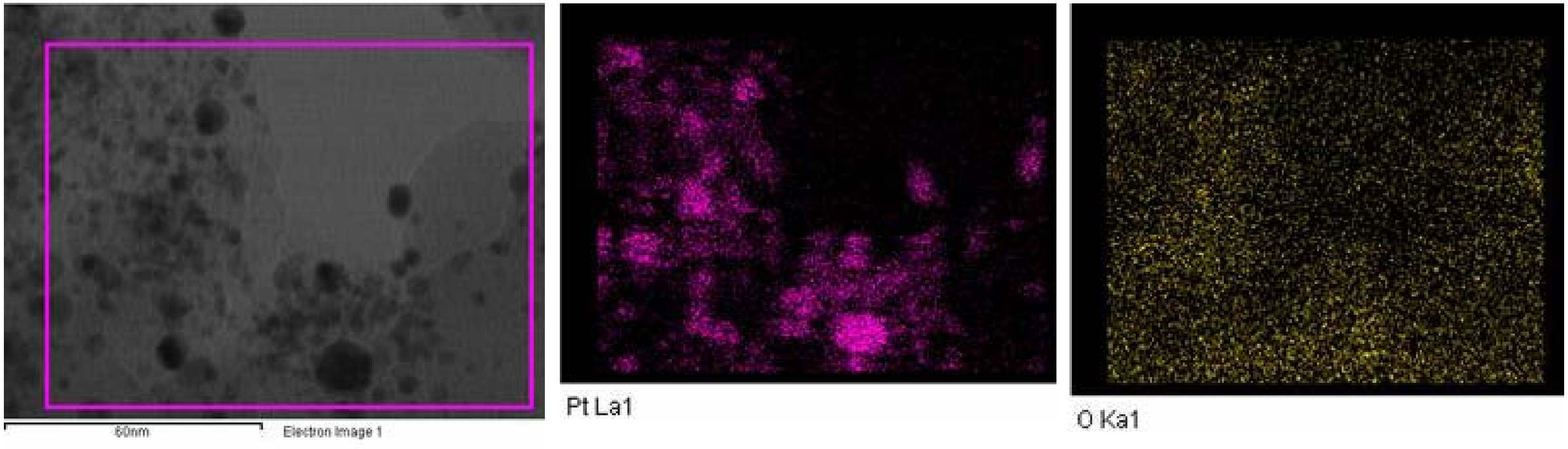


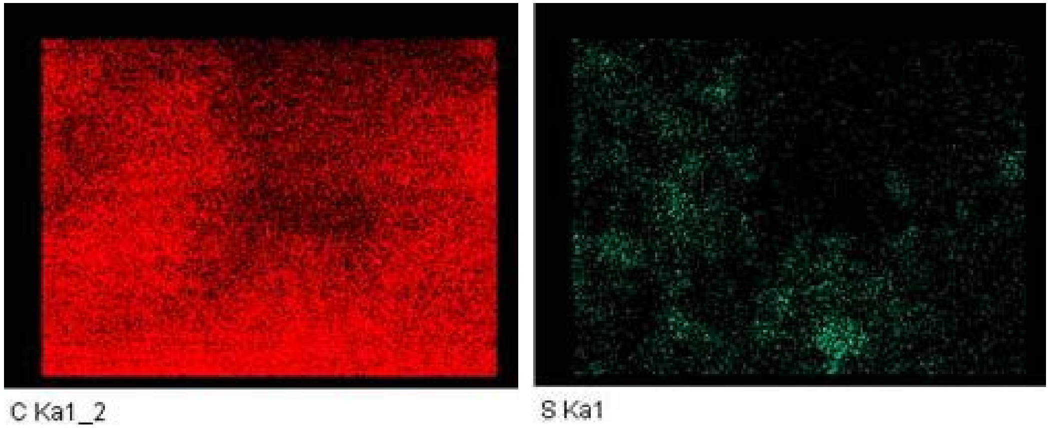

Pt La1
O Ka1
C Ka1_2
S Ka1

EDS shows that Pt, O, C and a small amount of S are present in fresh Pt/C.

20 wt% Pt/C

- **TEM & EDS - Reduced Pt/C:**

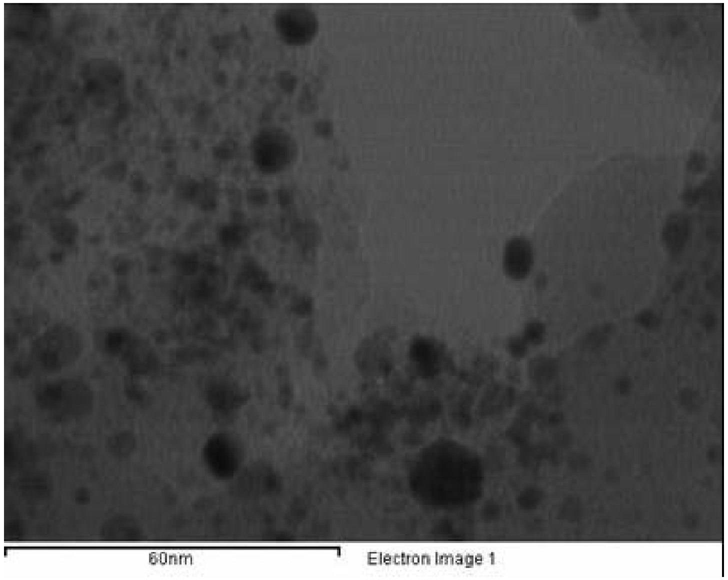




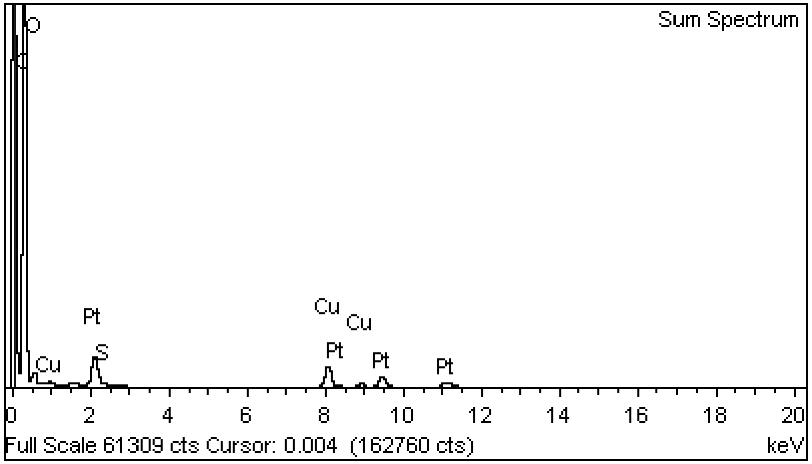
O, C and S are also present on reduced Pt/C.

20 wt% Pt/C

- **TEM &EDS-Reduced Pt/C:**



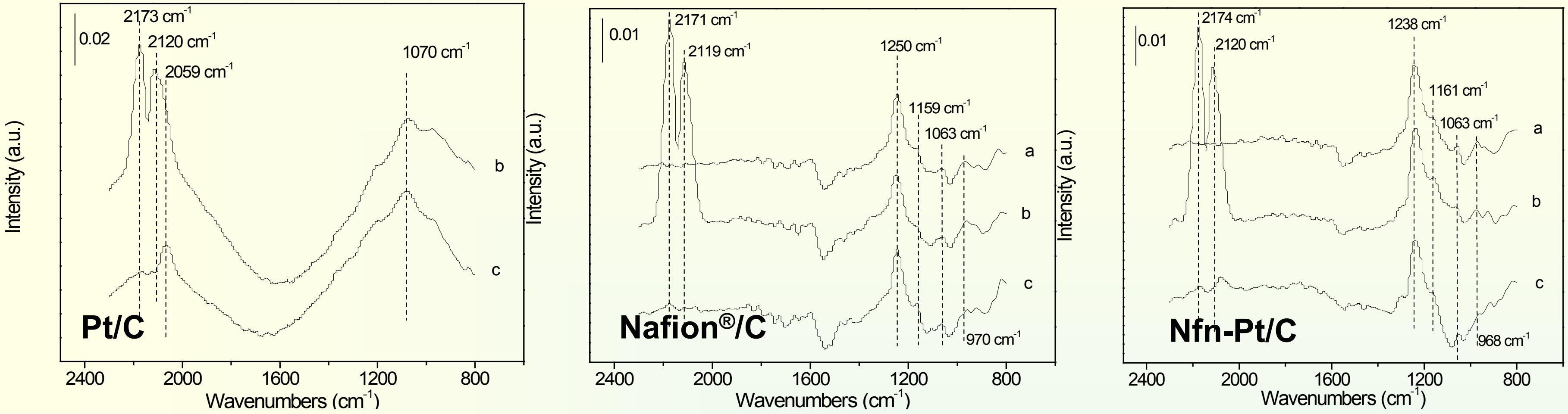
The amount of S on the reduced Pt/C is small.



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**

DRIFTS spectra of CO on Nafion®/C, Nfn-Pt/C, and 20 wt% 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 minimal effect of CO on the activity of Nafion®/C for esterification.**

IR band assignment

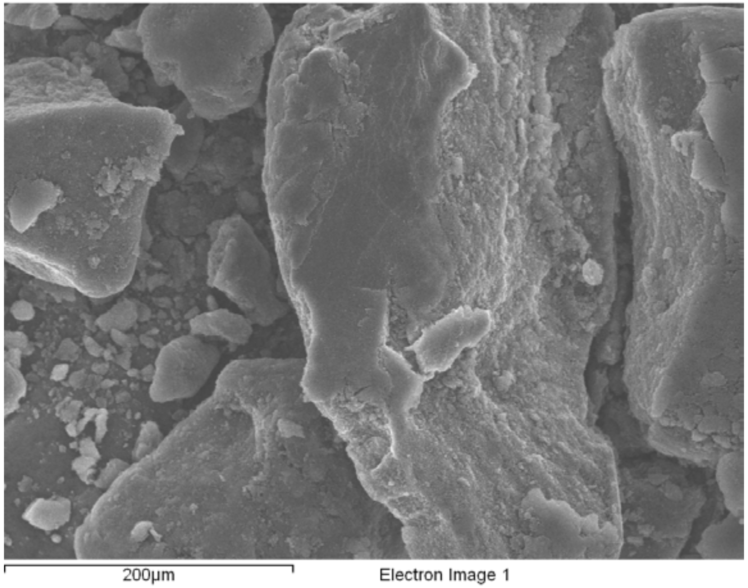
Wavenumber/cm^{-1}	Surface species
2171, 2119	gas phase CO
2059	linear CO
1250	CF_2 asymmetric stretching
1159	CF_2 symmetric stretching
1070	COH_x
1063	S-O symmetric stretching
970	C-O

- **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.

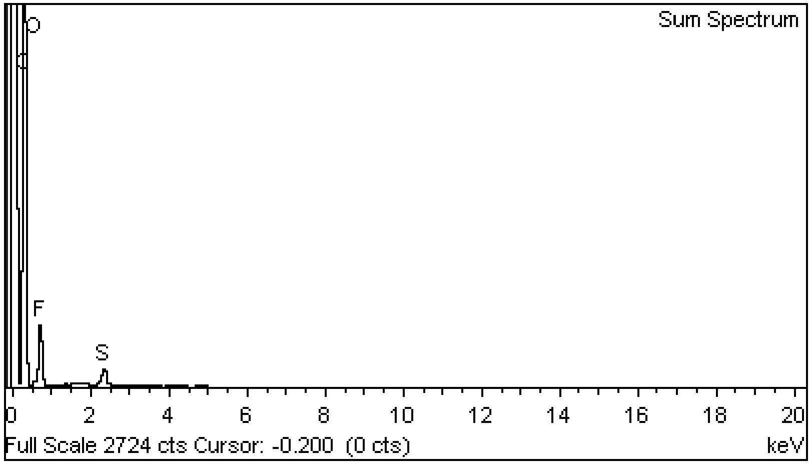
Nafion®/C

- **SEM & EDS:**



23% Nafion®/C

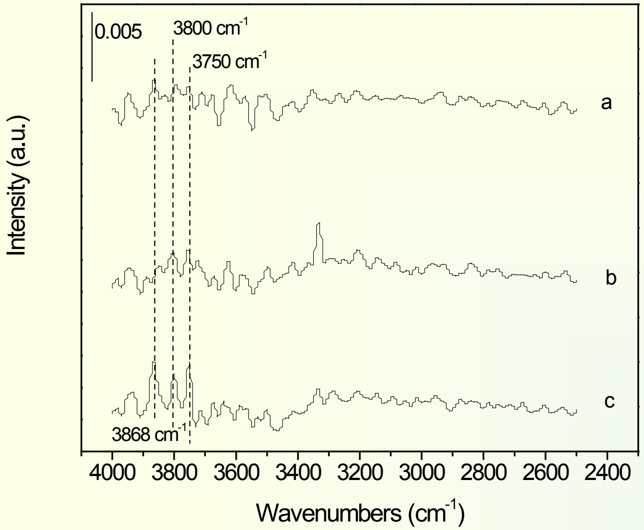
EDS of 23 wt% and 30 wt% Nafion®/C indicated that there are no significant impurities.

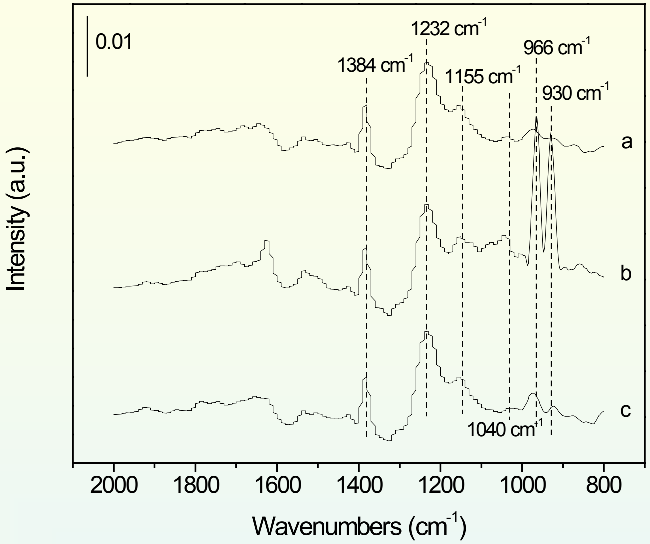


Element	Weight%	Atomic%
C K	74.7	82.2
O K	3.6	3.0
F K	20.7	14.4
S K	1.0	0.40
Totals	100.00	

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 adsorbed 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.**