“Effects of Impurities on Fuel Cell Performance and Durability”

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Specific DOE-FreedomCAR-Hydrogen technical barriers and technical targets that will be addressed

- Impact of impurities in H_2 and O_2 fuel streams on PEM fuel cell catalysts and operation

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Objectives of the Project

- **To determine the mechanism of the impurities in affecting the components of the fuel cell catalyst and polymer membrane.**
  - ***water***
  - ***hydrocarbons (including formaldehyde, formic acid),***
  - ***O_2***
  - ***inert gases (He, N_2, Ar)***
  - ***CO_2***
  - ***CO***
  - ***sulfur-containing gases***
  - ***ammonia***
  - ***halogenated compounds***
  - ***particulates***
- **To investigate the effect of impurities in the hydrogen fuel stream and the oxygen stream on the operation and durability of fuel cells.**
- **To delineate strategies/means to reduce the impact of these impurities.**

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Previous Research

- CO — **CO affects PEMFC anode for concentrations >10 ppm due to Pt poisoning.** *[Springer et al., J. Electrochem. Soc.148 (2001) A11]*
- CO_2 — **The effect varies from small to significant depending on the component and microstructure of the fuel cell anode probably due to reverse WGS.** *[Papageorgopoulos & De Bruijn,. J. Electrochem. Soc.149 (2002) A140]*
- NH_3 — **Trace NH_3 present in H_2 rich fuel streams degrades cell performances not by affecting Pt so much as the conductivity of the PEM.** *[Chellappa et al., Appl. Catal. A: Gen. 227 (2002) 231]*
- H_2S: — **Extensive poisoning of anode catalyst in PEMFC caused by 50 ppb of H_2S due to strong adsorption on Pt.** *[LANL, 2004]*
- SO_2 — **Even 500 ppb levels of SO_2 have acute and irreversible negative effects on FC cathode performance.** *[LANL, 2004]*
- Cl^- — **Little work has been carried out studying influence of halogenates on the performance of electrocatalysts of PEMFCs. The presence of Cl^- does not significantly affect catalyst activity, but NaCl decreases membrane conductivity.** *[LANL, 2004]*
- He, Ar, N_2 — **No electrode performance deterioration has been found related to inert gases such as He, Ar. N_2 could have an effect depending on the metal catalyst due to adsorption on the active sites and possibly formation of ammonia**. *[Zhu, J. Alloys and Compounds 240 (1996) L1]*

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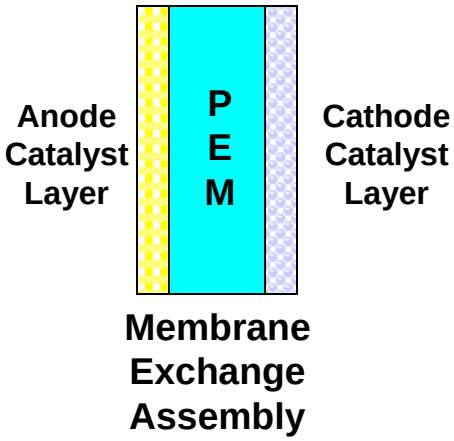
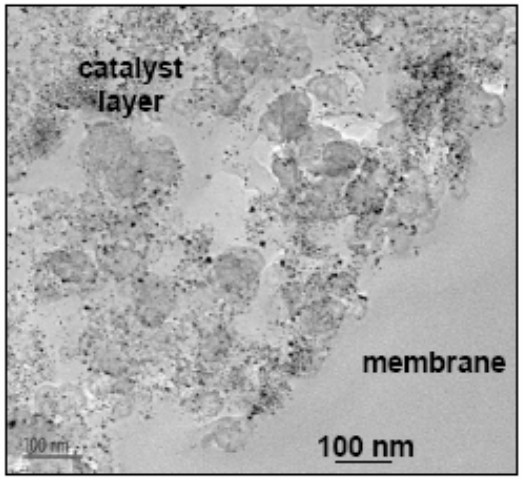
Approach

- TASK 1: MATERIALS ACQUISITION / PREPARATION

  (Clemson & SRNL)

  - ***Pt, PtRu Catalysts and PEM***
  - ***MEA***
  - ***Premixed Gases***





LANL, 2004

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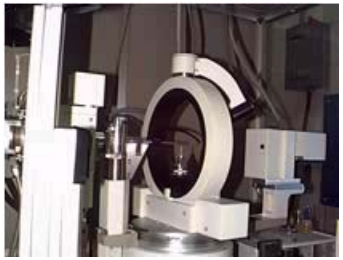
Approach

- TASK 2: STUDY OF IMPURITY EFFECTS ON Pt/C, Pt-Ru/C

(Clemson)



XRD

TEM

- *Surface Area/ Pore Volume/ Pore Size Distribution*
- *Transmission Electron Microscopy (TEM)*
- *EDX*
- *X-ray Diffraction (XRD)*
- *Hydrogen Chemisorption*
- *Impurity Adsorption*
- *FTIR*
- *Solid State MAS-NMR*
- *H_2/D_2 Exchange Reaction*
- *H_2+O_2 Reaction*

Adsorption

Impurity	Conc.
CO	0.1-1 ppm
CO_2	5-50 ppm
NH_3	0.05-0.5 ppm
Ethane	1-10 ppm
Ethylene	1-10 ppm
Formic Acid	0.1-1 ppm
Formaldehyde	5-50 ppb
O_2	2-20 ppm
H_2O	2-20 ppm
Cl_2	20-200 ppb
H_2S	2-20 ppb
He, Ar, N_2	50-500 ppm

Higher concentrations of impurities will also be used in the mechanism studies in order to magnify their effect.

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Approach

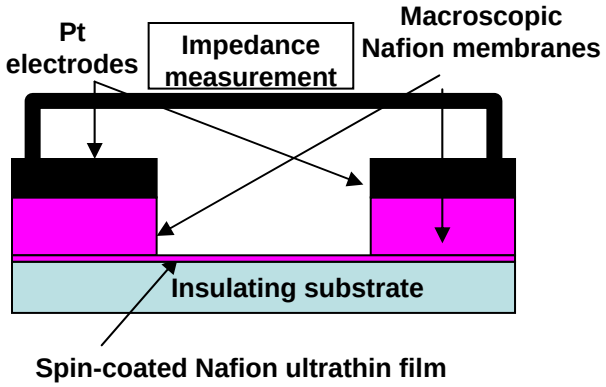
- TASK 3: STUDY OF IMPURITY EFFECTS ON NAFION

(Clemson)

TPR/TPD

FT-IR

- ***Impurity Adsorption***
- ***Surface Area/ Pore Volume/ Pore Size Distribution***
- ***Determination of the Bronsted Acid Sites***
- ***FTIR***
- ***Solid State MAS-NMR***
- ***Characteristic Acid-Catalyzed Reaction***
- ***Proton Conductivity***



Impurity	Conc.
CO	0.1-1 ppm
CO_2	5-50 ppm
NH_3	0.05-0.5 ppm
Ethane	1-10 ppm
Ethylene	1-10 ppm
Formic Acid	0.1-1 ppm
Formaldehyde	5-50 ppb
O_2	2-20 ppm
H_2O	2-20 ppm
Cl_2	20-200 ppb
H_2S	2-20 ppb
He, Ar, N_2	50-500 ppm

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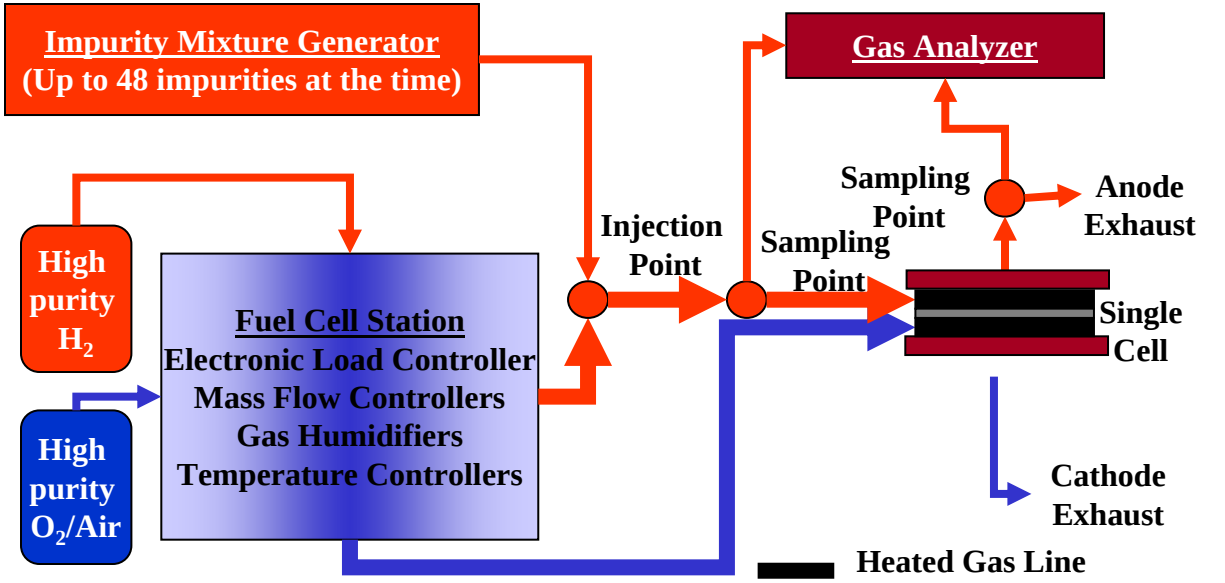
Approach

- TASK 4: PEM FUEL CELL PERFORMANCE TESTING

(SRNL & John Deere)

SRNL Test Equipment

Impurity	Conc.
CO	0.1-1 ppm
CO_2	5-50 ppm
NH_3	0.05-0.5 ppm
Ethane	1-10 ppm
Ethylene	1-10 ppm
Formic Acid	0.1-1 ppm
Formaldehyde	5-50 ppb
O_2	2-20 ppm
H_2O	2-20 ppm
Cl_2	20-200 ppb
H_2S	2-20 ppb
He, Ar, N_2	50-500 ppm



Temperatures (50°C, 90°C)
Pressures (P_a=P_c)(1 bar, 3 bar)
Humidity (100 % RH_{anode}, 50 % $RH_{cathode}$
Stoich. (A/C = 1.1/2.5 @1000 mA/cm$^{2)}$
Loading
Anode 0.2 mg Pt/cm^2 (45 wt% Pt-C)
Cathode 0.4 mg Pt/cm^2 (45 wt% Pt-C)
Electrolyte (Nafion® 111)
Cell Area (5 cm^2, 50 cm^2)
Current density (1000 mA/cm^2, 500 mA/cm^2)

12 kW PEM FC components
Available at end-of-life

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Project Timeline

Qtr	Materials 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 for cond. meas.	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 reaction*	*NMR*	Effect of CO:
	ANNUAL REPORT	ANNUAL REPORT	ANNUAL REPORT	ANNUAL REPORT

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Project Timeline

Qtr	Materials Acquisition /Prep.	Pt/C Study	Nafion Study	PEMFC Performance Testing
5	Prep. of Nafion membranes for cond. meas.	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:
	ANNUAL REPORT	ANNUAL REPORT	ANNUAL REPORT	ANNUAL REPORT
9	Go-No Go Decision	Go-No Go Decision	Go-No Go Decision	Go-No Go Decision

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Project Timeline

Qtr	Materials Acquisition /Prep.	Pt/C Study	Nafion Study	PEMFC Performance Testing
9	Prep. of Nafion membranes for cond. meas.	Effect of Ethane:	Effect of HCHO:	Effect of O_2:
10		Effect of HCOOH:	Effect of O_2:	Effect of HCOOH:
11		Effect of O_2:	Effect of HCOOH:	Effect of Cl_2:
12		Effect of H_2O:	Effect of Cl_2:	Effect of H_2O:
	ANNUAL REPORT	ANNUAL REPORT	ANNUAL REPORT	ANNUAL REPORT

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Project Timeline

Qtr	Materials Acquisition /Prep.	Pt/C Study	Nafion Study	PEMFC Performance Testing
13	Prep. of Nafion membranes for cond. meas.	Effect of Cl_2:	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

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Go/No-Go Decision Points

- **Delineation of mechanisms of effect on Pt and PtRu of CO, NH_3, and CO_2**
  - **Feb. 15, 2009**

- **Delineation of mechanisms of effect on Nafion of CO, NH_3, and CO_2**
  - **Feb. 15, 2009**

- **Delineation of the effect on Fuel Cell operation of CO, NH_3, and CO_2 and correlation to fundamental adsorption/reaction results on fuel cell catalysts and proton transfer membrane**
  - **Feb. 15, 2009**

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Organizations Responsible for Work

- **Clemson University**

  Dept. of Chemical and Biomolecular Engineering

  Clemson, South Carolina

- **Savannah River National Lab**

  Aiken, South Carolina

- **John Deere**

  Advance Energy Systems Division

  Charlotte, North Carolina

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Budget by Fiscal Year

Fiscal Year	Clemson University	SRNL	John Deere
FY07	$222,982 * *$130,505 ***	$145,402	*$37,500*
FY08	$296,118 *$84,787*	$193,867	*$50,000*
FY09	$301,431 *$43,275*	$193,565	*$50,000*
FY10	$307,630 $38,213	$193,701	*$50,000*
FY11	$77,265 $9,458	$48,445	*$12,500*

*DOE Funding **Cost-Sharing

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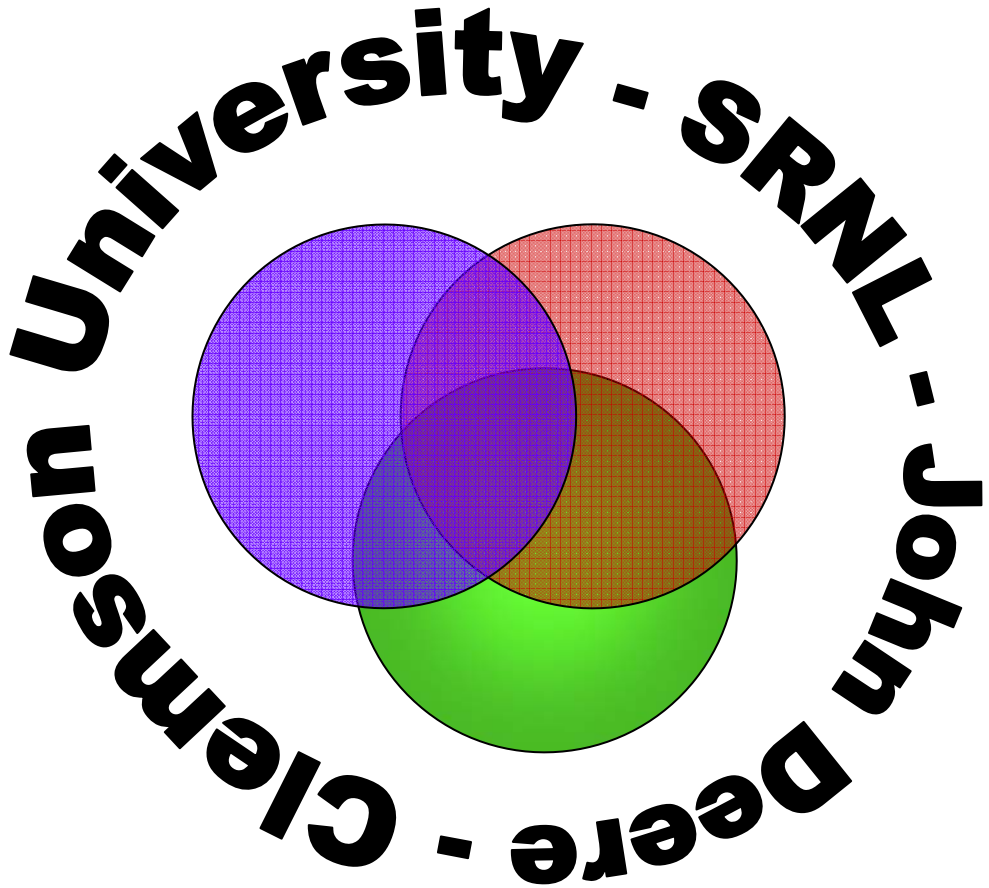

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